



A DICTIONARY  
OF  
APPLIED CHEMISTRY

VOL. IV.



A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

*Assisted by Eminent Contributors*

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# A DICTIONARY OF APPLIED CHEMISTRY

BY

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*ASSISTED BY EMINENT CONTRIBUTORS*

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IN FIVE VOLUMES

VOL. IV.

*WITH ILLUSTRATIONS*

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# ABBREVIATIONS

## OF THE TITLES OF JOURNALS AND BOOKS.

<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Annalen der Chemie (Justus Liebig).
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur.</i>	Annales de l'Institut Pasteur.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Bentl. a. Trim.</i>	Bentley and Trimen. Medicinal Plants.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen
<i>Bied. Zentr.</i>	Biedermann's Zentrallandwirtschafts-Betrieb. rationellen
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Brewers J.</i>	Brewers Journal.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Soc. Proc.</i>	Journal of the Chemical Society of London. Proceedings.
<i>Chem. Soc. Trans.</i>	Journal of the Chemical Society of London. Transactions.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.
<i>Färber-Zeit.</i>	
<i>Flück. a. Hanb.</i>	Pharmazie.
<i>Frühl.</i>	
<i>Gazz. chim. ital.</i>	Gazzetta chimica italiana.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i>	Journal of the Institute of Brewing.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Phys. Chem.</i>	Journal of Physical Chemistry.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers.</i>	Journal of the Society of Dyers and Colourists.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeit.</i>	Pharmazeutische Zeitung.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society.
<i>Phot. J.</i>	Photographic Journal.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Rec. trav. chim.</i>	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i>	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.



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# A

## DICTIONARY

### OF

## APPLIED CHEMISTRY.

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**OILSTONE.** A fine-grained hone-stone used with oil for sharpening edged tools. The most celebrated is the Turkey oilstone, an extremely hard and compact material, obtained in the interior of Asia Minor, and exported from Smyrna. It contains 70-75 p.c. silica, 20-25 p.c. calcium carbonate, and a little alumina. Two varieties are recognised, the white and the black, the latter being slightly the harder. In this country the Charley Forest stone has obtained great repute as an oilstone for whetting tools and penknives. It is a slaty rock, worked at Whit Forest, Leicestershire. The Welsh oilstone is a somewhat similar material, from near Llyn Idwal in North Wales, whilst the Devonshire oilstones are obtained from the neighbourhood of Tavistock. Several kinds of oilstone are worked in the United States. The Arkansas stone is a compact or fine-grained rock of bluish-white colour, used for delicate instruments, like those of surgeons and watchmakers. Somewhat similar, but more abundant, is the Washita oilstone, a white, opaque stone used chiefly by the Indians of the Washita (or Ouachita) river. The name 'novaculite' is also applied to the Arkansas and Washita stones. Their material consists almost entirely of chalcedonic silica (99.5 p.c.).

In preparing oilstones for use, the rough pieces are cut into regular shapes on the lapidary's wheel, fed with diamond powder, and are rubbed smooth with sand or emery on an iron plate. The slab of stone is in some cases cemented to a wooden base, by means of putty. Some of the stones are used not only for sharpening tools, but for finishing turned and planed surfaces of metal work. Oilstone powder is also employed for grinding the brass fittings of mathematical instruments (*v. R. Knight, Trans. Soc. Arts, 50, 233; C. Holtzapffel, Turning, vol. 3, 1081; and G. P. Merrill, The Non-metallic Minerals, 2nd edit., 1910; v. also Whetstones*).

F. W. R.

**OKRA,** also called gumbo; *Hibiscus esculentus* (Linn.), an annual plant bearing edible

Pods. Zega (Chem. Zeit. 1900, 24, 871) found as the average of 4 analyses—

Water	Protein	Fat	N-free extract	Fibre	Ash
80.7	4.2	0.4	12.1	1.2	1.4

According to American analyses (Bull. 28, U.S. Dept. of Agric. 1899), the edible portion of the pods, used largely as a vegetable in America, is much more watery, as shown by the following figures:—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
90.2	1.6	0.2	4.0	3.4	0.6

whilst, according to the same authority, canned okra contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94.4	0.7	0.1	2.9	0.7	1.2

(*v. also Tinsley, Amer. Chem. J. 1893, 14, 625*).

**OLD FUSTIC** is the wood of a tree known as the *Chlorophora tinctoria* (Gaudich), previously called *Morus tinctoria* (Linn.) which occurs wild in different tropical regions. The tree frequently grows to a height of over 60 feet, is exported in the form of logs, sawn straight at both ends, and usually deprived of the bark. The best qualities of old fustic come from Cuba and the poorer from Jamaica and Brazil. It is at the present time used very largely, and, together with logwood, is the most important of the natural dyestuffs.

The coloring matters of old fustic were first described by Chevreul (Leçons de chimie appliquée à la teinture, II. 150), who described two substances, one sparingly soluble in water, called *morin*, and a second somewhat more readily soluble. Wagner (J. pr. Chem. [i.] 51, 82) termed the latter *moritanic acid*, and considered that it possessed the same percentage composition as morin.

Annalen, 127, 351), on the other hand, found that the so-called moritanic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name 'Maclurin.'

**Morin**  $C_{15}H_{10}O_7 \cdot 2H_2O$ . To isolate this colouring matter from old fustic a boiling extract



of the rasped wood is treated with a little acetic acid and then with lead acetate solution. This causes the precipitation of the morin in the form of its yellow lead compound, whereas the main bulk of the maclurin remains in solution. The washed precipitate in the form of a thin cream is run into boiling dilute sulphuric acid, and the hot liquid, after decantation from the lead sulphate, is allowed to stand. Crystals of crude morin are gradually deposited, and a further quantity can be isolated from the acid solution by means of ether. During the preparation of commercial fustic extract, the solution on standing, or the concentrated extract itself, deposits, as a rule, a brownish-yellow precipitate, which consists principally of a mixture of morin and its calcium salt, and this forms the best source for the preparation of large quantities of the colouring matter. The precipitate is washed with a little boiling dilute hydrochloric acid to decompose the calcium compound, extracted with

of a little boiling water to the mixture.

Crude morin can be partially purified by crystallisation from dilute alcohol or dilute acetic acid, but the product usually contains a trace of maclurin. To remove the latter the finely powdered substance is treated in the presence of a little boiling acetic acid with fuming hydrobromic acid (or hydrochloric acid), which precipitates the morin as halogen salt, whereas the maclurin remains in solution (Bablich and Perkin, Chem. Soc. Trans. 1896, 69, 792). The crystals are collected, washed with acetic acid, decomposed by water, and the regenerated morin crystallised from dilute alcohol.

Morin crystallises in colourless needles (B. and P.), readily soluble in boiling alcohol, soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a bright orange-coloured precipitate and ferric chloride an olive-green colouration.

Loewe (Zeitsch. anal. Chem. 14, 112) was the first to assign to morin the formula  $C_{15}H_{10}O_7$ , and that this was correct was shown by the analysis of its compounds with mineral acids (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 649). The hydrochloride, hydrobromide, and hydriodide are obtained in orange-coloured needles, and possess the formulae  $C_{15}H_{10}O_7 \cdot HCl$ ,  $C_{15}H_{10}O_7 \cdot HBr$ , and  $C_{15}H_{10}O_7 \cdot HI$ , but the sulphuric acid compound, known as *anhydromorin sulphate*  $C_{15}H_8O_5 \cdot H_2SO_4$ , orange-red needles, is of an abnormal character. *Monopotassium morin*  $C_{15}H_9O_7 \cdot K$ , yellow needles, *monosodium morin*  $C_{15}H_9O_7 \cdot Na$ , *magnesium morin*  $(C_{15}H_9O_7)_2 \cdot Mg$ , orange-yellow needles, and *barium morin*  $(C_{15}H_9O_7)_2 \cdot Ba$ , orange crystalline powder, have also been prepared (Perkin, Chem. Soc. Trans. 1899, 75, 437).

When an alcoholic solution of morin is treated with bromine (Benedikt and Hazura, Monatsh. 5, 667; Hlaziwetz and Pfandler, J. 1864, 557) it is converted into *tetrabrom-morin ethyl ether*  $C_{15}H_5Br_4O_7 \cdot Et_2H_2O$ , colourless needles, m.p. 155° (Herzig, Monatsh. 18, 700), and this when digested with stannous chloride and hydrochloric acid gives *tetrabromo-morin*  $C_{15}H_5Br_4O_7$  (B. and H.), colourless needles,

m.p. 258°. According to Perkin and Bablich, this latter compound is more simply prepared by the direct bromination of morin suspended in acetic acid.

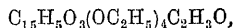
Morin forms few crystalline derivatives. By the action of acetic anhydride, according to the usual methods, a colourless amorphous product results, and a crystalline derivative has not yet been prepared.

However, converts the monopotassium salt of the colouring matter into *tetra-acetyl morin*  $C_{15}H_5O_3 \cdot (C_2H_3O)_4$ , colourless prismatic needles, m.p. 142°–145°, but this on further acetylation gives an amorphous compound.

Tetrabromomorin, on the other hand, yields a crystalline derivative (Bablich and Perkin, Chem. Soc. Trans. 1895, 67, 649), colourless needles, 192°–194°, and it was subsequently found by Herzig that tetrabromomorin ethyl ether yields the compound  $C_{15}HBr_4O_7 \cdot Et(C_2H_3O)_4$ , m.p. 116°–120°.

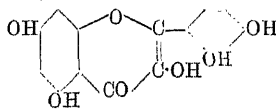
By fusion with alkali morin gives *phloroglucinol* (H. and P.), and *resorcinol* (B. and H.), whereas in this manner Bablich and Perkin isolated *β-resorcylic acid*. With acetic anhydride and methyl iodide morin yields *mono-acetyl morin*  $C_{15}H_9O_3(OCH_3)_1$  (B. and P.), colourless needles, m.p. 131°–132°, is produced, but is isolated with difficulty, and from this compound with alcoholic potash a yellow potassium salt, readily decomposed by water, is obtained. *Mono-acetyltetramethylmorin*  $C_{15}H_5O_3(OCH_3)_4 \cdot C_2H_5O$ , colourless needles, melts at 167°.

*Morin tetraethyl ether*  $C_{15}H_5O_3(OC_2H_5)_4$  (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 61), yellow needles, m.p. 126°–128°, and *acetylmorintetraethyl ether*

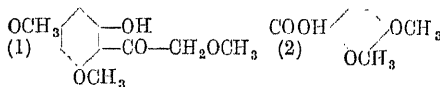


colourless needles, m.p. 121°–123°, could only be prepared in small quantity.

When *morin tetramethyl ether* is hydrolysed with alcoholic potash *β-resorcylic acid dimethyl ether*, and *phloroglucinolmonomethyl ether* are produced. Bablich and Perkin (Chem. Soc. Trans. 1904, 85, 61) give the constitution of a morin the constitution of a (tetrahydroxyflavonol)—



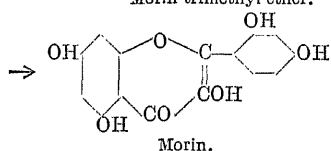
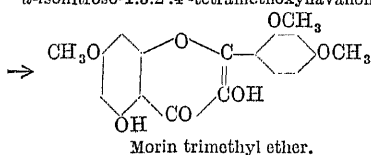
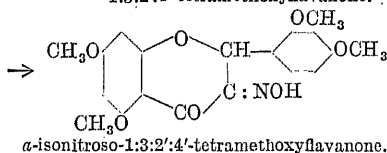
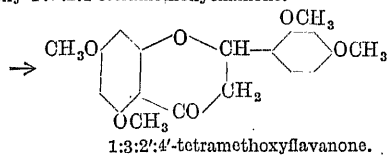
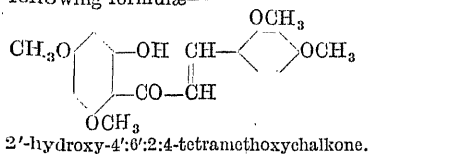
and that this formula correctly represents the substance, has been proved by its synthesis (Kostanecki, Lampe and Tambor, Ber. 1906, 39, 625), and also by the investigation of Herzig and Hofmann (Ber. 1909, 42, 155). It has been shown by the latter chemists that when morin is methylated by means of methyl sulphate *morin pentamethyl ether*  $C_{15}H_5O_2(OCH_3)_5$ , needles, m.p. 154°–157°, can be produced. This compound is hydrolysed with boiling alcoholic potash into *β-resorcylic acid dimethyl ether* (1), and *fisetol trimethyl ether* (1) (cf. QUERCETIN and FISETIN)—



the latter being identical with the compound

obtained in a similar way from quercetin pentamethyl ether.

Kostanecki, Lampe and Tambor (Ber. 1906, 39, 625) have synthesised morin by reactions similar to those found serviceable in the artificial preparation of fisetin and quercetin (see *YOUNG FUSTIC* and *QUERCITRON BARK*), but in this case the formation of the flavanone did not proceed smoothly and only a small quantity could be prepared. The synthesis is illustrated by the following formulæ—



Morin dyes mordanted woollen cloth shades which, though of a slightly stronger character, closely resemble those given by kaempferol.

	Chromium	Aluminium	Tin	Iron
Morin	Olive yellow	Yellow	Lemon yellow	Deep olive brown
Kaempferol	Brown yellow	„	Bright yellow	Deep olive brown

(Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 590).

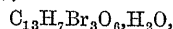
**Maclurin**  $C_{13}H_{10}O_6$ . When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the maclurin. The crude product is dissolved in dilute acetic acid (Perkin and Cope). A crude maclurin is also obtained during the preparation of fustic extract, partially in the form of its calcium salt, and this product is treated with dilute hydrochloric acid and crystallised from water. In order to decolourise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed,

and the solution is treated with sulphuretted hydrogen. The clear liquid is now much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

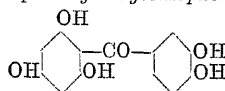
When quite pure maclurin consists of colourless needles, m.p.  $200^{\circ}$  (Wagner, J. 1850, 529), somewhat soluble in boiling water, soluble in alkalis with a pale yellow colouration. With aqueous lead acetate it gives a yellow precipitate and with ferric chloride a greenish-black colouration.

Hlasiwetz and Pfaundler (J. 1864, 558) assigned the formula  $C_{13}H_{10}O_6$  to maclurin, and found that by boiling with potassium hydroxide solution it gives *phloroglucinol* and *protocatechuic acid*.

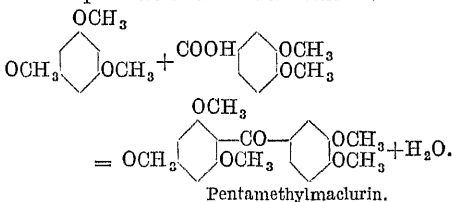
*Pentamethyl maclurin*  $C_{13}H_8O_6(C_2H_5O)_5$  melts (Kostanecki, Ber. 1894, 21, 1990); and *tribrom maclurin*



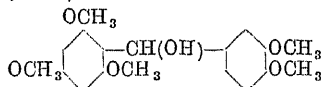
colourless needles has been obtained by Benedikt. *Maclurin pentamethyl ether*  $C_{13}H_5O(CH_3)_5$ , colourless leaflets, melts at  $157^{\circ}$ . König and Kostanecki first assigned to maclurin the constitution of a *pentahydroxybenzophenone*—



W. H. Perkin and Robinson (Chem. Soc. Proc. 1906, 22, 305), and somewhat later Kostanecki and Tambor (Ber. 1906, 39, 4022) synthesised maclurin pentamethyl ether, by the interaction of veratric acid and phloroglucinol trimethyl ether in presence of aluminium chloride—



When maclurin pentamethyl ether is digested with alcohol it gives *leucomaclurin-pentamethyl* (Kostanecki and Lampe, Ber. 1906, 39, 4014)



is produced in prismatic needles, m.p.  $109^{\circ}$ – $110^{\circ}$ , and this on further reduction gives *pentamethoxydiphenyl methane*, m.p.  $107^{\circ}$ – $108^{\circ}$ .

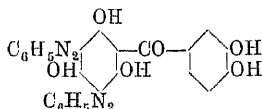
On the other hand, if leucomaclurin pentamethyl ether is oxidised in acetic acid solution, *veratric acid* and *dimethoxybenzoquinone* are formed.

Maclurin is interesting as it represents the *kinoid* type of compound, which is possible, however, that kinoin from Malabar kino, and aromadendrin from eucalyptus kino also belong to this class (v. KINO).

**Patent fustin.** Under the name of 'patent fustin' a colouring matter has been placed on

the market, which consists chiefly of disazobenzene maclurin (C. S. Bedford, 1887; Eng. Pat. 12667). To prepare this substance old fustic is extracted with boiling water, the solution is decanted from the precipitate of morin and its calcium salt which separates on cooling, and is neutralised with the necessary quantity of sodium carbonate. Diazobenzene sulphate is then added until a precipitate no longer forms, and this is collected and washed with water. It is sold in the form of a paste and dyes chrome mordanted wool an orange-brown shade.

**Disazobenzene maclurin** (Bedford and Perkin, Chem. Soc. Trans. 1895, 67, 933; *ibid.* 1897, 71, 186) which crystallises in salmon-red prismatic needles, m.p.  $270^{\circ}$  (decomp.) has the following constitution—



With acetic anhydride it gives *triacetyl disazobenzene maclurin*  $\text{C}_{15}\text{H}_5\text{O}_5(\text{C}_6\text{H}_5\text{N}_2)_2(\text{C}_2\text{H}_3\text{O})_3$ , in orange-red needles, m.p.  $240^{\circ}$ – $243^{\circ}$  (decomp.).

**Dyeing properties of old fustic.** In silk and cotton dyeing fustic is employed to a comparatively limited extent, but in wool dyeing it is the most important natural yellow dyestuff. The olive-yellow or old gold colours which fustic yields when used with chromium mordant and the greenish olives obtained with the use of copper and iron mordants are all fast to light and milling, but the yellow colours yielded in conjunction with aluminium and tin possess only a moderate degree of fastness with respect to light. Fustic is chiefly employed in wool dyeing with potassium dichromate as the mordant, and it is for the most part used along with other dyestuffs, e.g. logwood, alizarin, &c., for the production of various compound colours, olive, brown, drab, &c. A. G. P.

#### OLEFIANT GAS v. ETHYL.

**OLEFINES.** Hydrocarbons of the  $\text{C}_n\text{H}_{2n}$  series homologous with ethylene.

**OLEIC ACID v. OILS, FIXED, AND FATS;**  
SAPONIFICATION.

**OLEIN v. OILS, FIXED, AND FATS;**  
GLYCERIN.

#### OLEOMARGARINE v. MARGARINE.

**OLEO-RESINS.** Under the generic term oleo-resins are here described the chief representatives of that large group of natural products the essential constituents of which are resin and volatile oil. These substances are, for the most part, the oleo-resinous juices of plants more or less deprived of their volatile oil by evaporation, but still retaining enough for it to rank as one of their two leading components. For a more detailed list of oleo-resins, the numerous reports on botanical economics, and the catalogues of the various museums, should be consulted. Compare also the introduction to the article on RESINS.

**Copaiba.** *Oleo-resin copaiba*; *Balsam of copaiba* or *copaiva* or *cupivi*; (*Baume ou oléorésine de copaiba*, Fr.; *Copaiba balsam*, Ger.). Copaiba is the oleo-resinous secretion of the trees of the genus *Copaifera*, especially the species *C. Lansdorfii* (Desf.), which inhabit the warmer districts of South America. Descriptions

of the leading species yielding the so-called balsam are given by Flückiger and Hanbury (Flück. a. Hanb. 227) and Benth. a. Trim. 93. The drug became known in Europe in the seventeenth century, and was included in the Amsterdam Pharmacopœia of 1636 and the London Pharmacopœia of 1677. The yield of oleo-resin from a single tree is very great, the ducts containing it distending sometimes to such an extent as to burst the bark. In commerce the Pará variety is distinguished from that coming from Maranhão and from the rarer Maracaibo copaiba.

In trade the oleo-resin occurs as a transparent, rarely liquid of a pale-yellow or colour, and a characteristic disagreeable, odour and persistent acid bitterish taste. The specific gravity, which varies with the proportion of oil present, is generally 0.94 to 0.993. Alcohol, benzene, carbon disulphide, or acetone dissolve most specimens of copaiba: glacial acetic acid dissolves the resin only. When mixed with small quantities of magnesia, lime, or baryta, most specimens form a stiff mixture which hardens. This depends upon an acid resin which forms solid with alkaline earth metals. Flückiger (Jahresb. Pharm. 1867, 162; 1868, 140) finds the action of copaiba on polarised light to vary, some specimens being dextro- and others levorotatory.

The *volatile oil* in copaiba varies from 20 to 80 p.c., the percentage of *resins*, which are the sole other constituents, showing corresponding differences. A method for the estimation of the volatile oil is given by Cripps (Pharm. J. [iii.] 22, 193).

*Volatile oil* of copaiba or *copaivene*  $\text{C}_{20}\text{H}_{32}$  is an isomeride of oil of turpentine. It boils at  $252^{\circ}$ – $256^{\circ}$ , is soluble in 8 to 30 parts of alcohol (sp.gr. 0.830), or in 3 parts of absolute alcohol, and has a sp.gr. of 0.88 to 0.91. The oil has the odour and taste of copaiba. When hydrochloric chloride is passed into the dried oil, crystals of *copaivene hydrochloride*  $\text{C}_{20}\text{H}_{32}\cdot 4\text{HCl}$  are formed (Levy and Engländer, Annalen, 242, 191). Cf. Bonastre (J. Pharm. 11, 529); Ader (*ibid.* 15, 95); Gerber (Br. Arch. 30, 157); Blanchet (Annalen, 7, 156); Soubeiran and Capitaine (J. Pharm. 26, 70); Aubergier (*ibid.* 27, 278); Gerhardt (Compt. rend. 17, 314); Chautard (*ibid.* 34, 485); and Posselt (Annalen, 69, 67). The terpene of Maracaibo copaiba boils at  $250^{\circ}$ – $260^{\circ}$ , and gives *copaivene hydrochloride* (Brix, Monatsh. 2, 187). *hydrate* ( $\text{C}_{20}\text{H}_{32}\cdot 3\text{H}_2\text{O}$ ) is obtained towards the end of the operation when the moist terpene is distilled over sodium (Brix).

The oil from copaiba balsam collected in Surinam from (Desf.) boils, for the most part, appears to be a mixture of two *sesquiterpenes*. The fraction boiling at  $270^{\circ}$ – $280^{\circ}$  contains a little cadinene. Towards the end of the steam distillation of the balsam, a *sesquiterpene alcohol*  $\text{C}_{15}\text{H}_{26}\text{O}$ , m.p.  $114^{\circ}$ – $115^{\circ}$ , separates in the condenser from which a *sesquiterpene*  $\text{C}_{15}\text{H}_{24}$ , b.p.  $252^{\circ}$ , is obtained. The latter is a mobile liquid which soon changes in the air to a resinous solid (van Itallie and Nieuwland, Arch. Pharm. 242, 539; 244, 161).

*Adulteration of copaiuba* has been largely practised. Turpentine, castor oil, and gurjun balsam, are typical of the adulterants employed. Numerous methods of testing have been proposed. These are reviewed by Siebold (Pharm. J. [iii.] 8, 251). It is shown that the specific gravity or percentage of resin and oil is so variable as to be of no value in detecting adulteration. Many properties while appertaining to most specimens of the oleo-resin are not found in all. Thus fluorescence, a character of gurjun balsam, is not absent from all speci-

During the sixteenth century, the older African elemi was replaced by a drug of similar

appearance, which came from Mexico, and South America, and this in its turn has given way to a product of the Philippine Islands, which is now the elemi of commerce.

*Elemi or Animi of the older Writers; Oriental or African Elemi; Luban Meyeti; Luban Mati.*

This drug is derived from *Boswellia Frereana* (Birdwood), a tree belonging to the same genus which yields the gum-resin olibanum, and which inhabits the hills immediately west of Cape Gardafui. Notwithstanding the close botanical relation to *olibanum*, the generic name, Luban being Arabic for that drug, there is no doubt, owing to the entire absence of gum and other characters, that Luban Meyeti is a distinct product. According to Hanbury and Flückiger (Pharm. J. [iii.] 8, 805; Flück. a. Hanb. 147), this was the elemi of commerce until its place was taken, in the sixteenth century, by a somewhat similar product of Mexico and South America.

Luban elemi is described by Flückiger and Hanbury as detached dropy tears and fragments, occasionally in stalactitic masses several ounces in weight. Externally it has a thin, opaque white crust, but internally it is transparent and of an amber colour. It has an agreeable odour of lemon and turpentine, and a mild terebinthinous taste. The volatile oil, which has a fragrant elemi odour, from the specimen examined, amounted to 3.1 p.c. It has a specific gravity of 0.856 at 17°, and rotates the polarised ray slightly to the left. It consists partly of a dextrorotatory hydrocarbon  $C_{10}H_{10}$ , and partly of a levorotatory oxygenated oil. The resin is mostly soluble in alcohol, and has the composition  $C_{20}H_{30}O_2$ .

*Elemi of the Seventeenth and Eighteenth Centuries; American or Brazilian Elemi.*

The oleo-resin, which replaced the older African elemi for the most part during the seventeenth and eighteenth centuries, was the product of several Brazilian trees, species of the genus *Protium* (Jacq.). A specimen examined by Flückiger and Hanbury (Pharm. J. [iii.] 152), was a transparent, yellowish, terebinthinous resin, which by means of cold spirits of wine could be separated into two portions—the one soluble, and the other consisting of a mass of acicular crystals, the latter soluble (Ann. Chim. Phys. [iii.] 13, 166) investigated one of the *Leuca* oleo-resins which had lost all its volatile oil, and consisted of three neutral compounds, which he separated by the difference of their solubility in alcohol. From the alcoholic solution, *brea* first comes out in white pearly stellate needles, melting at 157°. *Brea* has the composition C 83.92 p.c., H 11.82 p.c., and O 4.26 p.c. In sulphuric acid it dissolves with a red colour. Further concentration of the alcoholic solution yields crystals of *icacin*, which contain C 82.01 p.c., H 11.64, and O 6.35 p.c. From the mother-liquor a small quantity of an amorphous resin, *colophon*, was obtained.

The oleo-resin of *Protium heptaphyllum* (March.), was examined by Stenhouse and Groves (Chem. Soc. Trans. 29, 175). This is known as *Gum Hyauca*, or *Ogima resin*, or *resin of the incense-tree*. It possesses a fragrant balsamic odour,

which depends on the presence of a small proportion of volatile oil. This oil, when obtained by distillation with steam, boils at about 270°. By treatment with sodium and fractional distillation, it gives a hydrocarbon *contine*,  $C_{15}H_{24}$ , which boils at 264°. If the residue, after removal of the volatile oil, be dissolved in hot alcohol, it deposits on cooling a crystalline compound, *icacin*,  $C_{46}H_{76}O$ , and the mother-liquor contains a yellow amorphous resin. *icacin* melts at 175° (cf. Hesse Annalen, 192, 181). A comparison of the analytical numbers, melting-points, and other characters, points to the probability that while the *icacin* of Scribe is only an impure form of that observer's *brea*, this, in its turn, is the *icacin* of Stenhouse and Groves in an imperfect condition of purity. The amorphous resin of the latter observers is also probably the *colophon* of Scribe. At all events, the evidence of the existence of *brea* and *icacin* needs revision.

*Elemi of Commerce of the Present Day; Manilla Elemi; Arbol a Brea Resin.*

The tree which yields the elemi of the present day is a native of the Philippine Islands, and is called by the natives *Arbol a Brea*. Its botanical relations were not known until quite recently, but it is now certain that the oleo-resin is collected from *Canarium luzonicum* (Miq.), (Clover, Philippine J. Sci., 1907, 2, 2). *Manilla elemi* is a soft oleo-resin which, in appearance, resembles old honey. It occurs in commerce generally admixed with earthy or carbonaceous matter, which gives it a dark colour. When fresh and pure, it is colourless and has a fragrant odour. Cold spirits of wine applied to the drug discloses numerous acicular crystals visible under a microscope (Flück. a. Hanb.).

Elemi is a mixture of volatile oil and resin. The volatile oil contains *d*-phellandrene, dipentene, and a crystalline compound which may be identical with amyryn (Wallach, Annalen, 252, 102). Phellandrene and dipentene are also obtained by the dry distillation of the resin (Wallach, *ibid.* 271, 310).

The resin of elemi was first examined by Maujean (J. Pharm. 9, 45), who showed that it contains two resins, one soluble in cold and the other in hot alcohol. Cf. Rose (Annalen, 13, 192; 32, 297; 40, 307) and Hesse (*ibid.* 29, 136). Bonastre (J. Pharm. 10, 199) found the former to exist to the extent of 61 p.c., and the latter, which crystallised easily, 25 p.c. Baup (Ann. Chim. Phys. [iii.] 31, 108) called the latter *amyryn*. It is insoluble in water, readily soluble in ether and hot alcohol, and crystallises in satiny fibres, which melt at 174° (Baup) or 177° (Flück. a. Hanb.). Cf. Buri (Neues Rep. Pharm. 25, 193) and Hesse (Annalen, 192, 180). *Amyryn*,  $C_{30}H_{50}O$ , has been converted by Vesterberg into two crystalline isomeric acetates,  $C_{30}H_{48}(C_2H_3O_2)$  and benzoates,  $C_{30}H_{48}(C_7H_5O_2)$ , from which two corresponding *amyryns* have been prepared. *α*-*Amyryn* melts at 181°–181.5°, (*α*)-*amyryn acetate* at 220° and *benzoate* at 192°; while *β*-*amyryn* melts at 193°–194°, (*β*)-*amyryn acetate* at 235°, and *benzoate* at 230° (Ber. 20, 1243; 23, 3186). Ciamician (Ber. 11, 1347), by distilling amyryn with zinc-dust, obtained toluene, methylethylbenzene, and ethyl-naphthalene.

The alcoholic mother-liquor contains the *amorphous resin*, or resin soluble in cold alcohol, which is *elemi*. Besides amyryrin, her compounds occurring in elemi—*breydin*, *brein*, and *bryoidin*. Brein is certainly, in view of Flückiger and Hanbury's investigation, impure amyryrin (cf. Vesterberg, Ber. 39, 2467), and the existence of breidin requires further proof.

*Elemi* have been Cremer (Arch. Pharm. f the drug contain: *manamyryrin*, consisting of  $\alpha$  and  $\beta$  amyryrin, 20–25; essential oil, 20–25; *bryoidin*, 0.8–1;  $\alpha$ -*maneletic acid*, 5–6;  $\beta$ -*maneletic acid*, 8–10; *mancleresene*, 30–35; inorganic constituents and bitter substance, 1–2; impurities, 5–6 parts. Bryoidin,  $C_{21}H_{42}O_8$ , m.p. 135.5°, was prepared by digesting the elemi with dilute alcohol at a gentle heat and evaporating the extract to crystallisation. It is neutral, has a bitter taste, and, whilst insoluble in cold water, dissolves readily in hot water and in alcohol and ether (Pharm. J. [iii.] 5, 142).  $\alpha$ -Maneletic acid  $C_{27}H_{50}O_4$ , m.p. 215°, previously isolated by Buri (Pharm. J. [iii.] 8, 601), crystallises from the alcoholic solution of the acids, extracted from the resin by aqueous

mother-liquor containing  $C_{44}H_{90}O_4$ ,  $C_{18}H_{30}O$  remains after the removal of the other constituents of the oleo-resin; it is amorphous and melts at 63°–65°.

Elemi is seldom used in medicine in this country. It is, however, sometimes employed in the form of ointment as a dressing for indolent ulcers. At present its chief use is in the preparation of printing inks, and occasionally as an ingredient in varnishes.

#### Oleo-resins allied to Elemi.

*Anime*. Much confusion exists as to the use of the word anime, and the same may be remarked of *tacamahac*. By some writers anime is used as synonymous with elemi, and by others it is restricted chiefly to a variety of copal. There are, however, a number of other oleo-resinous products which are usually known as anime. The chief members of this class are:—1. *Gomart oleoresin*, the exudation of *Dacorydes*, an inhabitant of the West Indies (Imp. Inst. Rep. No. 63, 192). This has an odour between that of elemi and turpentine. Owing to its general resemblance to true elemi, gommier resin is commonly known as 'dry' or West Indian elemi. For analysis and commercial valuation, see Imp. Inst. Report. The oleo-resin has been examined by More (Chem. Soc. Trans. 75, 718). The essential oil was found to contain 64 p.c. of l-pinene and 17 p.c. of sylvestrene, and from the resin a crystalline  $C_{27}H_{50}O_4$ , 166°–167°, was obtained, having  $C_{27}H_{50}O_4$ . 2. *Brazilian anime*, the product of *Hymenaea Courbaril* (Linn.), a tree belonging to the natural order *Leguminosae*. The oleo-resin resembles mastic. It softens in the mouth, and when warmed emits a peculiar odour. The volatile oil is colourless, with a strong, not unpleasant odour and burning taste. It is completely soluble in alcohol (Paoli, Brugn. Giorn. 16, 326). After removal of the oil, cold alcohol extracts an

*amorphous resin*, and the residue, dissolved in boiling alcohol, deposits on cooling a *semi-crystalline compound*, which was analysed by Laurent (Ann. Chim. Phys. [ii.] 66, 314). See also Batka (Pharm. J. [iii.] 6, 742); Guibourt (Rév. scient. 16, 177); Filhol (J. Pharm. Chim. [iii.] 1, 301, 507); Hancock (Ed. N. J. Sc. 1, 240); Manzini (J. Pharm. 27, 752); Deville (Annalen, 71, 354).

*Curana*. A soft oleo-resin allied to Brazilian elemi, probably derived from *Protium Carana* (March.) and allied species. It has a fragrant balsamic odour and somewhat bitter taste. It contains 96 p.c. of resin, soluble in alcohol (Pelletier, Bull. Pharm. 4, 241). Carana elemi from *Protium Carana* (March.), has been examined by Tschirch and Saal (Arch. Pharm. 241, 149), who found that in 100 parts of the drug there were contained *isocareleminic acid*, 2; *careleminic acid*, 8; *careleminic acid*, 10; essential oil, 10; amyryns, 20–25; resene, 30–35; impurities, 12–15 parts. For analytical constants v. Dieterich (Pharm. Centh. 40, 453).

*Ceradia*. The product of *Ceradia (Othonna) furcata* (Lindl.). It is an amber-coloured oleo-resin with the odour of elemi (R. Thomson, Phil. Mag. 28, 422).

*Mauritius elemi*. An oleo-resin very closely allied to *Curana*. It is the yield of the (Blume; Flück. a. Hanb. 152). It has been examined by Tschirch and Saal (Arch. Pharm. 242, 348). 100 parts of the drug were found to contain  $\alpha$ -*isocolelemic acid*, 10; *colelemic acid*, 2;  $\beta$ -*isocolelemic acid*, 8; *colamyryrin*, 25–30; *coleresene*, 30–35; essential oil, 3; *elemi*, 10; and bryoidin, plant remains and 10 parts.

*Mexican elemi*. *Vera Cruz elemi*. Mexican elemi is not now an article of commerce. It is nearly related to Brazilian elemi. It is the reputed product of *Myrsine* (DC.); (Flück. a. Har. 152). It has been examined by Tschirch and Cremer (Arch. Pharm. 240, 293), who find that it contains a very large proportion of substances which resist the action of alkalis (resene and amyryrin) and this would make it peculiarly suitable for the basis of a lacquer.

*Tacamahac*. The following are the more important oleo-resins which have been described as *tacamahac*:—1. *East Indian tacamahac*, the product of *Calophyllum Inophyllum* (Linn.), which inhabits Bourbon and Madagascar. It is a dark-green balsamic resin—sp.gr. 1.032; m.p. 75°. 2. *Yellow tacamahac*, the exudation of *Amyris tacamahac* (Batka). It was labelled *Tacamahague verge* by Des Marchais, *African incense* by Pereira, and *Bellium d'Afrique* by Guibourt. It melts at 100°, exhaling an agreeable odour, and the resin remaining is partly soluble in alcohol. The part insoluble in alcohol consists of yellow crystals—*tacamahacin*. This substance is insoluble in ether, sparingly soluble in alcohol, and is unaffected by alkalis or nitric acid. Sulphuric acid dissolves it with a violet colour (Batka, Pharm. J. [iii.] 6, 742). Yellow *tacamahac* is often termed anime. 3. *Oleo-resin of Protium heptaphyllum* (Aub.). This has been already described under the name of *conima resin* (see *Elemi of the seventeenth and eighteenth centuries*). A number of samples of *Tacamahaca* resin have been examined by Tschirch and Saal (Arch. Pharm. 242, 365, 395).

and analytical constants are given by Dieterich (Pharm. Centh., 40, 453).

Besides these, which Batka regards as true *tacamahacs*, the product of *Prolium Obusifolium* (March), the *Mauritius tacamahac*, and common *galipot* of *Pinus Pinaster* (Soland), the latter under the name of the *bitter tacamahac* of trees, have been described as varieties of that drug.

**Gurjun oleo-resin.** *Gurjun balsam*; *Wood oil*; *Oleo-resina dipterocarpi*. This oleo-resin resembles and is used as an adulterant and substitute for copaiba. It is obtained from Burma and the Straits, being the product of various species of *Dipterocarpus* (Flück. a. Hanb. 88). Gurjun oil must not be confounded with the fatty oil which is also known as wood oil, or *wood oil of China*, which is expressed from the seeds of the *Aleurites cordata* (Steud.), the well-known *Tung* tree of the Chinese.

Gurjun, or wood oil, resembles copaiba in appearance, with the exception of its fluorescence, a character rarely found in copaiba. When heated in a closed tube to 220° it becomes almost solid, whereas copaiba similarly heated does not lose its fluidity. For other distinguishing characters v. COPAIBA.

Wood oil was examined by Lowe (Pharm. J. 13, 65); Hanbury (*ibid.* 15, 321); Martius (Neues Rep. Pharm. 5, 100); Guibourt (*ibid.* 6, 97), and Hirschsohn (Pharm. J. [iii.] 10, 561). Werner (Zeitsch. Chem. 1862, 588) found it to consist of 20 p.c. of *volatile oil*  $C_{20}H_{42}$ , a polymeride of turpentine, and a residual resin which contained *gurjunic acid*  $C_{44}H_{88}O_8$ , a crystalline compound soluble in aqueous ammonia. Other observers have found different percentages of oil and resin, which are indeed variable. The volatile oil boils at 255°–260° (Flück. a. Hanb.), 255° (Werner), and its sp.gr. is 0.915 (Flück. a. Hanb.); 0.904 (Werner); 0.928 (De Vry, Pharm. J. [iii.] 16, 374). Amyl alcohol dissolves the volatile oil, but it is only sparingly soluble in ethyl alcohol, and glacial acetic acid. The hydrocarbon is coloured a magnificent blue by hydrochloric acid, but does not form a crystalline hydrochloride.

When the resin of wood oil is extracted by alcohol and aqueous solution of ammonia added, and the *amorphous resin* which separates collected, the solution contains *ammonium gurjunate* from which gurjunic acid is obtained as a precipitate on the addition of a mineral acid, and it may then be recrystallised from ether or alcohol. Werner found it to melt at 220°, and to boil with decomposition at 260°. Gurjunic acid is soluble in alcohol, benzene, and carbon disulphide. It may be regarded as tri-hydrated abietic acid thus:  $-C_{44}H_{88}O_8 \cdot 3H_2O$ . This formula agrees equally well with Werner's data. It is probably identical with the meta-copaibic acid of Strauss (v. COPAIBA). A compound,  $C_{20}H_{30}O_2$ , yielding a diacetate is obtained from gurjun oleo-resin and enters commerce as 'copaibic acid.' It is crystalline, melts at 126°–129°, is soluble in alcohol and ether but insoluble in water and alkalis (Brix, Monatsh. 2, 516). The amorphous resin which constitutes the chief part of the resin of wood oil consists of *gurjoresene*  $C_{17}H_{28}O_2$ , m.p. 40°–43° (Tschirch and Weil, Arch. Pharm. 241, 372). The deposits, largely crystalline in

character, which are found in various samples of gurjun balsam, consist of resin-alcohols or resin phenols, but are insoluble in alkalis, in these respects resembling myrrin.

In addition to its use as a substitute for copaiba, wood oil is employed in India as a natural varnish, especially for ships.

**Labdanum**; *Ladanum*. A sticky, black-brown, soft oleo-resin, derived from *Cistus* (Willk.) and other species of the Grecian Archipelago and the shores of the Mediterranean (cf. Benth. a. Trim. 24). It is a variable mixture of resin, volatile oil, gum, wax, and earthy and woody impurities. The odour is fragrant, and it has a bitter taste. Guibourt (Hist. Drogues, 3, 601), Pelletier (Bull. Pharm. 4, 503), Johnston (Phil. Trans. 1840, 344), Thielton Dyer (Pharm. J. [iii.] 15, 301; 16, 385, 779). For analytical constants, see Dieterich (Pharm. Centh., 40, 453).

**Lupulin.** *Lupulinic gland* line, Fr.; *Hopfendrüse*, G. The detached minute glands of the strobile of *Humulus Lupulus* (Linn.) contain *volatile oil*, a *bitter acid*, *resin*, *wax*, and possibly an *alkaloid*.

Commercial lupulin has been examined by Barth (Chem. Zentr. 1900, [ii.] 681), who found it to contain 18.27 p.c. of ash, 63.93 p.c. of material soluble in ether and 36.07 p.c. of lupulin husks. The portion soluble in ether contained 0.18 p.c. of wax, 11.55 p.c. of *α-resin*, 43.31 p.c. of *β-resin*, 0.17 p.c. of ash, and 8.72 p.c. of fat oil, *γ-resin*, &c. The proportion of sand in commercial lupulin varies from 10.9 to 20.2 p.c.

The volatile oil which exists to the extent of about 0.9 p.c. (Flück. a. Hanb. 553), consists according to Wagner (J. 1853, 516) and Personne (J. Pharm. Chim. [iii.] 26, 241, 321; 27, 22; J. 1854, 654) of a *terpene*,  $C_{10}H_{16}$ , boiling at 175°, and an oxygenated compound probably *valerol*,  $C_8H_{16}O$ , which boils at 210° and on oxidation yields *valeric acid*. The latter acid has also been detected in hops. The crude oil boils from 140°–300°. Cf. Mehu (Thèse, Montpellier, 1867), and Ossipow (J. pr. Chem. [ii.] 28, 448). Chapman (Chem. Soc. Trans. 67, 54, 780) finds that the oil can be separated into two fractions: one, boiling at 166°–171°, probably a mixture of two *hydrocarbons*,  $C_{10}H_{16}$  and  $C_{10}H_{18}$ , and the other, a sesquiterpene, *humulene*,  $C_{15}H_{24}$ , b.p. 160°–170° (60 mm.). The latter gives a crystalline nitroschloride, melting at 164°–165°.

The resins present in lupulin are divided into soft and hard resins, according as they are soluble or insoluble in light petroleum (Hayduck, Bied. Zentr. 1887, 694). The *α-resin*, a soft resin precipitated by lead acetate, contains *α-lupulinic acid*, which, when pure, is extremely resistant to oxidation, but is transformed into *β-lupulinic acid* (Chem. Zentr. 1888, 18, 21). The *β-resin*, a soft resin, is not precipitated by lead acetate. It appears to be an oxidation product of an organic acid, *β-lupulinic acid*, first obtained from hops by Bungerer (Bull. Soc. chim. [ii.] 45, 489). To prepare lupulinic acid, lupulin is extracted with light petroleum and the crude crystals which are obtained on concentrating the solution are purified by recrystallisation from alcohol and

afterwards from light petroleum. The acid crystallises in glistening prisms which melt at 92° and become resinous on exposure to air (Barth and Lintner, Ber. 31, 2022). The  $\gamma$ -resin is insoluble in light petroleum. Siller (l.c.) finds it to be a mixture of at least two distinct resins differing in carbon content and in solubility in ether.

**Mecca or Opobalsam.** *Balm of Gilead.* This oleo-resin is the balm of the Old Testament and the Greek writers, and is the substance to which the name 'balsam' was originally applied. The term has, however, with the advance of discovery, come to have another meaning, and is now employed in a generic sense for those resins, oleo-resins, or gum-resins which contain cinnamic or benzoic acids (compare BALSAMS). Mecca oleo-resin is the product of *Commiphora Opobalsamum* (Engl.), a tree growing in Arabia. Trommsdorff (N. J. T. 16, 62) finds it to consist of *volatile oil*, 30 p.c.; *soft resin insoluble in alcohol*, 4 p.c.; *hard resin soluble in alcohol*, 64 p.c. A specimen analysed by Bonastre (J. Pharm. 18, 95) contained only 10 p.c. of volatile oil, and the other constituents were correspondingly higher. In physiological action, the oleo-resin is allied to copaiba and the turpentine.

**Hardwickia pinnata oleo-resin.** This oleo-resin is an Indian substitute for copaiba. It is derived from a tree nearly related to the *Copaifera*, which inhabits the forests of South Travancore Ghats and South Canara. A specimen examined by Flückiger and Hanbury (Flück. a. Hanb. 233) was a thick, black-looking, viscid fluid, which, when viewed by transmitted light in thin layers, was yellow-green or vinous red, according to the thickness. It had no fluorescence, nor was it gelatinised by heating, as is the case with wood oil. Broughton (Beddows, Flora Sylv. S. India, Madras, 1872, 255) found 25 to 40 p.c. of *volatile oil* ( $C_{10}H_{18}$ ), boiling at 225°. From the resins this observer was unable to prepare copaivic acid.

**Minjak-lagam.** An oleo-resin resembling gurjun was examined by Haussner (Arch. Pharm. 21, 241). It is dingy green by reflected and yellow by transmitted light. It is soluble in alcohol, ether, benzene, chloroform, or carbon disulphide, and yields 33 p.c. of *volatile oil*  $C_{20}H_{32}$ , boiling at 250°. The resin is composed of an acid  $C_{17}H_{14}O_2$  and a neutral constituent.

**Sumbul oleo-resin** (*Racine de sumbul*, Fr.; *Sumbulwurzel*, *Moschuswurzel*, Ger.). The root of *Ferula Sumbul* (Hooker), or musk root (Bentl. a. Trim. 131), a perennial plant, inhabiting the mountains of Maghian, in the Khanate of Bokhara. When extracted with ether it yields about 9 p.c. of a resin, having a musky odour and  $\frac{1}{2}$  p.c. of a bluish *volatile oil*.

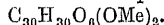
Reinsch (Jahrb. pr. Pharm. 6, 300; 7, 79; 13, 68), by dissolving the resin in alkali and precipitating with water, obtained a salt of *sumbulamic acid*, together with some *angelate*, the two being separated by the easier solubility of the latter in water. Free sumbulamic acid is a turpentine-like mass, which assumes the form of soft yellow needles on standing. Compare also Reinsch and Riecker (Jahrb. pr. Pharm. 16, 12). The existence of an alkaloid *sumbuline* in the resin has not been confirmed (cf. Murawieff, Dub. Quart. J. 1852, 255). Sommer (Arch. Pharm. 138, 1) investigated sumbul root. On dry dis-

tillation, the oleo-resin gives first a *greenish mobile oil*, smelling like creosote, then a *blue oil*, lighter than water, and with a peculiar, not very agreeable, odour. Together with these, the same observer found crystals of *umbelliferone*.

**Turpentine.** The oleo-resinous exudates of various species of *Conifera*.

*Crude or common turpentine.* This is derived in Russia and Finland from the *Pinus sylvestris* (Linn.), or Scotch pine; in Austria and Corsica from *P. Laricio* (Poiret); in South-Western France from *P. Pinaster* (Solander); and in the United States from *P. palustris* (Mill.), the swamp pine and the Loblolly pine, *P. Taeda* (Linn.) (Flück. a. Hanb. 604; Bentl. a. Trim. 256-259). Tschirch and Niederstadt (Arch. Pharm. 239, 167), using the method of examination of resins already described, find the oleo-resin from *Pinus sylvestris* contains: *silvolic acid*, 1.5; *silvinoic acids*  $\alpha$  and  $\beta$ , 58-60; *essential oil*, 15; *silvoresene*, 20-21; bitter substance, succinic acid, and impurities, 1-2 p.c. (cf. Schkateloff, Chem. Zentr. 1908, i. 2097).

The resin from *Pinus laricio* (Poiret), Austrian turpentine, melts at about 100° and has a yellow colour which on exposure to light becomes red. On boiling with water for a long time and then extracting with ether, caffeic and ferulic acids were obtained and also vanillin (Bamberger, Monatsh. 12, 479). The resin is resolved on digestion with ether into an  $\alpha$ -modification (80 p.c.), which is soluble in ether, and a  $\beta$ -modification (20 p.c.) insoluble in ether. When excess of potash is added to an alcoholic solution of the  $\alpha$ -resin or of the crude resin, a colourless crystalline potassium compound is formed which, when treated with hydrochloric acid, gives a powdery precipitate of *pinoresinol*. The caffeic and ferulic acids are in all probability present in an uncombined state (Bamberger, Monatsh. 15, 605). Pinoresinol can be obtained by heating  $\alpha$ -resin at 122°, and has the composition  $C_{30}H_{30}O_4(OMe)_2$ . The  $\beta$ -resin, on purification, forms a chocolate brown powder and appears to have the composition



Its properties are those of a tannol whence it is named *pinoresinolannol* (Bamberger and Landsiedl, Monatsh. 18, 481). Tschirch and Schmidt (Arch. Pharm. 241, 570) found 100 parts of the oleo-resin to contain: *laricopinic acid*, 25; *laricopinonic acid*, 34; *essential oil*, 35; *resen*, 2; water, bitter substance and impurities, 3-4 parts.

Tschirch and Brüning (Arch. Pharm. 238, 630) find in Bordeaux turpentine, the oleo-resin of *P. Pinaster* (Solander), 6-7 p.c. of *pinaric acid*  $C_{20}H_{30}O_2$ , crystals, m.p. 144°-146°; 48-50 p.c. of  $\alpha$ - and  $\beta$ -*pinarolic acids*; 28-30 p.c. of *essential oil*; 5-6 p.c. of *resene*; and 1-2 p.c. of *succinic acid*, *alkaloid*, *colouring matter*, *water*, and *impurities*. For concreted French turpentine, common frankincense or galipot, see RESINS.

*Pinus palustris* (Mill.) is the 'long leaf pine' of the United States and is the chief source of the turpentine and resin prepared there. In 100 parts of the oleo-resin, there are contained: *palabietic acid*  $C_{18}H_{20}O_2$ , m.p. 110°; 5; *palabietic acid*,  $C_{20}H_{30}O_2$ , m.p. 153°-154°; 6-7; *palabietinolic acids*,  $C_{18}H_{24}O_2$ , 53-57;



essential oil, 20-22; *paloresene*, 10; bitter substance, impurities, and water, 2-3 parts (Tschirch and Koritschoner, Arch. Pharm. 240, 568).

*Canada turpentine*, *Canada balsam*, *Balsam of fir*. A product of the balsam or balm of Gilead fir, the *Abies balsamea* (Mill.). This is incorrectly called balsam, and it must not be confounded with true balm of Gilead or Mecca balsam (cf. Fluck. a. Hanb. 612; Benth. and Trim. 263). A similar turpentine is obtained from the hemlock spruce, *Tsuga canadensis* (Carr.). This has been investigated by Tschirch and Brüning (Arch. Pharm. 238, 487). 100 parts of the turpentine contain *canadic acid*  $C_{19}H_{34}O_2$ , m.p.  $135^{\circ}$ - $136^{\circ}$ , 13; *canadolic acid*  $C_{19}H_{34}O_2$ , crystalline, m.p.  $143^{\circ}$ - $145^{\circ}$ , 0.3;  $\alpha$ - and  $\beta$ -*canadinolic acids*,  $C_{19}H_{34}O_2$ , m.p.  $89^{\circ}$ - $95^{\circ}$ , 48-50; essential oil, 23-24; *canadorene*, 11-12; succinic acid and impurities, 1-2 parts. The oleoresin also contains an alkaloid soluble in water. On dry distillation, formic, acetic, and succinic acids are formed.

*Venice turpentine*, *Larch turpentine*. The exudate of the larch *Larix decidua* (Mill.), mostly obtained from the Tyrol. Tschirch and Weigel (Arch. Pharm. 238, 387) have isolated *luricinolic acid*,  $C_{20}H_{30}O_2$ , m.p.  $147^{\circ}$ - $148^{\circ}$  crystals, 4-5 p.c.;  $\alpha$ - and  $\beta$ -*lurinic acids*  $C_{19}H_{28}O_2$ , which may be identical, 55-60 p.c.; essential oil, 20-22 p.c.; resene, 14-15 p.c.; alkaloid, colouring matter and impurities 2-4 p.c.; succinic acid, 0.1 p.c. (cf. Bamberger, Monatsh. 18, 481; Bamberger and Landsiedl, *ibid.* 20, 755).

*Strassburg turpentine* is the yield of the Silver fir (*Sapin*, Fr., *Weisstanne* or *Edeltanne*, Ger.), *Abies pectinata* (DC.). The market is supplied chiefly from the Vosges (Flück. a. Hanb. 615; Benth. a. Trim. 262). In 100 parts the turpentine contains *abietic acid*  $C_{19}H_{20}O_2$ , m.p.  $114^{\circ}$ - $115^{\circ}$ , 8-10; *abietric acid* crystalline,  $C_{20}H_{28}O_2$ , m.p.  $145^{\circ}$ - $153^{\circ}$ , 1.5-2;  $\alpha$ - and  $\beta$ -*abietinolic acids*, 46-50; essential oil, 28-31; *abietoresene*, 12-16; alkaloid, colouring matter, water, and impurities, 1-2; succinic acid, 0.05-0.08 parts (Tschirch and Weigel, Arch. Pharm. 238, 411).

*Hungarian turpentine* is obtained from the *Pinus Pumilio* (Haenke).

*Chian turpentine* is the turpentine of the older writers, and is derived from a small tree, *Pistacia Terebinthus* (Linn.), which inhabits the shores of the Mediterranean and Asia Minor.

*Jara turpentine* is the product of *Picea excelsa* (Link.). The resin melts at about  $100^{\circ}$  and when boiled with water gives an aqueous extract which contains *p-coumaric acid* and vanillin (Bamberger, Monatsh. 12, 441). Tschirch and Brüning (Arch. Pharm. 238, 616) isolated *piceapimaric acid*  $C_{20}H_{30}O_2$ , crystals, m.p.  $144^{\circ}$ - $145^{\circ}$ , 2-3 p.c.; *piceapimaric acid*  $C_{19}H_{28}O_2$ , 1.5-2 p.c.;  $\alpha$ - and  $\beta$ -*piceapimaric acids*  $C_{25}H_{44}O_2$ , 48-50 p.c.; essential oil, 32-33 p.c.; *javoresene*, 10-12 p.c.; succinic acid, alkaloid, colouring matter, water, and impurities, 1-2 p.c. (cf. Tschirch and Koch, Arch. Pharm. 240, 272).

The resin from *Pinus halepensis* (Mill.) is used in Greece for medicinal and flavouring wine. It has been investigated by Tschirch and Schulz (Arch. Pharm. 245, 166).

The resin oil from *Pinus longifolia* (Roxb.), a tree indigenous to the lower Himalayas, forms

a white rather tough opaque mass and has a granular structure which is due to the partial crystallisation of the resin acid. Its odour is extremely pleasant and somewhat resembles that of limonene. Distilled with steam it yields 18.5 p.c. of essential oil (Rabak, Chem. Zentr. 1905, [ii.] 896).

The resins of the Norway pine, *Pinus resinosa* (Solander) and the Douglas fir, *Pseudotsuga Douglasii* (Carr.), have been investigated by Frankforter (J. Amer. Chem. Soc. 28, 1467; 31, 561). Russian 'white pitch,' which is probably the product of *Abies sibirica* (Ledeb.), or of *Picea obovata* (Ledeb.) has been examined by Tschirch and Koritschoner (Arch. Pharm. 240, 584). Brooks (Philippine J. Sci. 1910 [A] 5, 229, has examined the oleo-resin of *Pinus insularis* (Endl.) and the resinous saps from various pines have been investigated by Schkateloff (Chem. Zentr. 1908, i. 2097).

#### Tar or TURPENTINE.

A. S.

**OLIBANOL**  $C_{25}H_{44}O$  is an alcohol contained in frankincense oil. It forms a yellow oil with an odour of frankincense, b.p.  $217^{\circ}/20$  mm.,  $333^{\circ}$ - $334^{\circ}/757$  mm.; sp.gr. 0.9596 at  $20^{\circ}$ ;  $n_D^{20}$  -1.750. When warmed with an equal weight of zinc chloride it yields a green oil, b.p.  $315^{\circ}$ - $318^{\circ}/749$  mm.; sp.gr. 0.9400 at  $20^{\circ}$ .

It is not attacked by alkaline potassium permanganate, but is completely decomposed by chromic acid (Haensel, Chem. Zentr. 1908, i. 1837; *ibid.* ii. 1436).

#### OLIVE, the fruit of *Olea europaea* (Linn.).

Many varieties are known. The fruit is largely used as a source of olive oil (*v. OLIVE OIL*). It usually consists of about 80 p.c. of flesh and rind, 17.5 p.c. of stone, and 2.5 p.c. of seed. All parts of the fruit contain oil, but the best is obtained from the flesh. According to König, the following gives the average composition of the various parts of the fruit:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Flesh	30.1	5.2	51.9	10.5	2.3
Stone	9.2	3.5	2.8	83.3	1.1
Seed	10.6	18.6	31.9	36.7	2.2

whilst the ash has the following percentage composition:—

	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Flesh	80.9	7.5	7.5	0.2	0.7	1.3	1.1	0.7	0.2
Stone	58.8	6.6	7.5	0.4	0.8	16.7	3.3	1.3	4.7
Seeds	30.3	2.0	30.4	1.2	0.1	28.2	2.4	5.4	0.1

The fruit has an insipid, bitter taste, and is usually pickled before being eaten, salt and spices being used for the purpose. The following are American analyses of the edible portions of pickled olives:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Green olives	58.0	1.1	27.6	11.6	1.7
Ripe olives	64.7	1.7	25.9	4.3	3.4

Ground olive stones or 'poivrette' have been used to adulterate pepper (*v. Wynter Blyth, Foods*; also Martelli, Staz. Sper. Agrar. 1895, 28, 53). For results of the examination of olive leaves and bark *v. Canzoneri* (Gazz. chim. ital. 1906, 36, [ii.] 372) and Power and Tutin (Chem. Soc. Trans. 1908, 93, 891, 904). According to Bourquelot and Vintilescu (Compt. rend. 1908, 147, 533), olives contain a glucoside—

*oleocuropein*—a yellow powder with bitter taste, hydrolysable by emulsin, which is present in the fruit, leaves, and bark, yielding dextrose (v. also Power and Tutin, *Pharm. J.* 1908, [iv.] 27, 714; and Vanzetti, *Atti. R. Accad. Lincei*, 1909, 18, ii. 188). H. I.

**OLIVE OIL.** Olive oil is obtained from the fruits of the olive tree, *Olea europaea (sativa)*, L. The olive tree is probably indigenous to Western Asia, but was at an early date introduced into all the countries bordering on the Mediterranean. Recently the cultivation of the olive tree has been introduced into California, South Africa, and Australia. The olive tree thrives best in a sub-tropical climate, and its successful cultivation extends in Europe as far north as latitude 44°. In America, it scarcely extends to latitude 34°. Attempts have also been made in several parts of India to cultivate the olive tree, but although it grows well and flowers, the fruit seldom matures.

The olives intended for oil production are gathered just before the period of maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully ripe or over-ripe fruits.

The proportion of oil in the fruit goes on increasing to the maximum found in fruit which has reached complete maturity; it then decreases slowly. The ripe olives contain up to 70 p.c. of oil. This figure is, however, an exceptional one, the fleshy part of the best cultivated olives containing only from 40 to 60 p.c. of oil. The Algerian olives vary in their proportion of oil within wide limits, from 10.03 p.c. to 32.98 p.c. (in the Jemmap olives). The Californian olives also yield much smaller quantities of oil than the best cultivated European varieties.

The technical processes employed for the production of olive oil are still represented by both the oldest and crudest processes (see preparation of OILS, FIXED, AND FATS) and by the most modern methods adapted to large-scale working.

The very finest oils are obtained from hand-picked fruits by first crushing them in a mill the kernels. Exceptionally prepared by peeling hand-pressing lightly, after carefully rnels. The crushed marc is a hydraulic press; the oil so obtained ranks as the best edible oil—*huile vierge*, *huile surfine*. Commercial brands of this quality are 'Provence Oil,' 'Aix Oil,' 'Nice Oil,' 'Var Oil.' The oils sold as 'Finest Tuscan Cream,' 'Riviera Oils' (Genoa), 'Bari Oils' may also be ranked amongst the best edible oils, although they are distinctly lower in value than the oils of the South of France, and come nearer the following somewhat inferior quality. This is obtained by pouring some cold water on the marc, after the pressure in the hydraulic press has been released, and pressing again. Such inferior oil is also sold as an edible oil, either alone or mixed with the oil of the first expression as *'Salad Oil,' 'huile fine,' 'huile de table ordinaire.'*

The pulp left in the press yields, after mixing with hot water and pressing once or twice, a bright oil used for lubricating purposes, as burning oil, and for soapmaking.

In most of the smaller works, the kernels are not removed and are crushed together with the fruit. In large establishments, however, the kernels are removed and the oil is pressed from olive kernel oil.

(AND FATS). The repeatedly pressed pulp (*'grignons'*) still contains a considerable amount of oil, varying from 10 to 22 p.c. This pulp is beaten with hot water in special mills—*moulins de runners*. The oil cells together with the water, is then.

into a series of vessels, arranged in tiers, where the water separates from the oil and broken cellular tissues. The oil and the tissue rise to the surface, to be skimmed off, whilst the heavier crushed kernels fall to the bottom. The latter are known as *'grignon marc blanc.'* The emulsion of oil and cellular tissue, which has been skimmed off, known as *'grignon marc noir,'* is heated and subjected to a fresh expression in a hydraulic press. The oil so obtained is termed *'huile de ressence,'* and the pressed residue is known as *'tourteau de ressence.'* The *huile de ressence* is allowed to rest in large tanks at a somewhat elevated temperature, when a clear oil separates on the top—*'huile claire de ressence'*—and a lower layer of thicker oil 'Olive Oil Grease' (*pâte de ressence*) settles out.

In some establishments the marc, instead of being boiled with water, is thrown into pits where the pulp undergoes a process of fermentation, whereby the oil gradually rises to the top. Oil of this kind is known as *'huile d'enfer.'* The name *'huile d'enfer'* is applied also to oil which has settled out from the waters obtained from the press after moistening and boiling the pulp, which has been stored in underground cisterns (*'enfes'*). To this class of oil belong the bagassa (bagasse) oils, which are obtained principally in Portugal from fermented marc. These oils contain as much as 60–70 p.c. of free fatty acids.

*'Tournant oil'* is a commercial product of the quality of the *'huiles d'enfer,'* obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 p.c.) of free fatty acids, and therefore forms a very complete emulsion (which constitutes its value) with a solution of sodium carbonate. Such Turkey-red oil was first employed for this purpose by Haussmann, 1792, and then recommended by Koechlin Frères.

The cake remaining after the removal of the *huile de ressence*, termed *'tourteau de ressence,'* or *'sanza,'* is finally deprived of its last content of oil by the use of solvents, sometimes after a second pressing. The solvent usually employed in France and Italy is carbon disulphide. Hence, these oils are termed 'sulpho-carbon oils,' 'sulphur olive oils.' They have a deep green colour, due to the chlorophyll which has been extracted by the solvent, and contain the more solid portion of olive oil which has remained behind in the pulp. These oils contain large proportions of free fatty acids as also notable amounts of lactones.

For the physical and chemical characteristics see tables OILS, FIXED AND FATS.

Some Tunisian olive oils are so rich in glycerides of solid fatty acids that they deposit

'stearine' ... they are unsuitable for ... such Tunisian oils must be 'demargarinated' (see OILS, FIXED, AND FATS).

The extracted cake is sold as manure. The press residues which have yielded superior kinds of olive oil, would be suitable for feeding cattle; but as the oil, which can be easily recovered by extraction—about 10 p.c. of the residues—is too valuable, olive cakes are only used locally and to an inconsiderable extent as cattle food.

Olive oil typifies eminently a non-drying oil. On account of its comparatively high price, it is adulterated to an enormous extent. How far the blending of various olive oils of different qualities should be considered as an adulteration must be decided in each given case. Undoubtedly the 'finest Nice oil,' which has been prepared by blending a genuine Nice oil with Tunisian oils or other olive oils, must be considered as of inferior quality. At present, olive oil is most frequently adulterated with arachis oil, as the latter offers greater difficulties to the analyst than those oils which were previously used to a much greater extent, viz. cotton seed oil, sesamé oil (rape oil). The adulteration with these oils has practically ceased for the time being; they are too easily detected. J. L.

**OLIVINE.** An abundant rock-forming mineral consisting of magnesium orthosilicate with variable amounts of ferrous orthosilicate,  $(Mg, Fe)_2SiO_4$ . Crystals are orthorhombic, but of rare occurrence; granular masses are more common. The colour is yellowish-green to black, depending on the amount of iron present. The mineral is decomposed by hot hydrochloric acid with separation of gelatinous silica. It occurs in many basic and ultra-basic rocks of igneous origin (basalt, gabbro, peridotite, &c.), and it is an important constituent of stony meteorites. Deposits of diamond, platinum, chromite, and nickel-ores are usually associated with olivine-rocks; and by the weathering of these rocks, serpentine and associated deposits of steatite, magnesite, and meerschbaum are formed. The only direct practical application of olivine is as a gemstone; the clear, colourless variety is yellowish-green (chrysolite) or reddish-brown (peridot) in colour. Such material comes mainly from the island of St. John in the Red Sea, and it is also collected from ant-hills in Arizona and New Mexico. L. J. S.

**OMEIRE.** A drink resembling koumiss, prepared by the natives in South-West Africa by filling gourd bottles, which contain some fermented milk, with milk, shaking well and allowing to stand. It is a thick, creamy liquid, possessing a pleasant, slightly sour taste; it contains a little alcohol (Arch. Pharm. 1887, 744).

**OMEROL** v. SYNTHETIC DRUGS.

**ONION SKINS.** The outer dry skins of the bulb of the onion, *Allium Cepa* (Linn.), were formerly employed for dyeing purposes. According to Leuchs (Farben und Färbekunde, 1825, i. 434), the outer skins of onion bulbs, which are of a yellowish-brown colour, have long been used in dyeing. Baster eggs yellow and in conjunction with alum for

dyeing woollen, linen and cotton materials. The colour is fast and particularly brilliant.

The dyestuff present is in reality *quercetin*, and this can be isolated from the skins to the extent of 1.3 p.c. by mere extraction with boiling water (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1295). A. G. P.

**ONOFRITE** v. MERCURY; also SELENIUM.

**ONONIS ROOT.** Contains a glucoside *ononin*  $C_{25}H_{30}O_{11}$ , forming colourless needles, m.p. 210°, decomposed by dilute acids into dextrose and *ononelin* (v. Hemmelmayr, Monatsh. 1902, 133; 1903, 132).

**ONYX.** A variety of chalcedonic silica differing from agate only in the straightness and absence of its differently-coloured layers, and is used for engraving as cameos. The alternate bands of colour are usually white and black, or white and red; in sardonyx they are white and brown. Most of the onyx with intense differences in colour, as now placed on the market, has been coloured artificially by chemical means (v. AGATE). L. J. S.

**ONYX-MARBLE.** Algerian onyx, Mexican onyx, or 'Oriental alabaster' (also called 'onyx' in ancient times and in the marble trade of the present day). A banded, translucent variety of fibrous or granular calcite, or marble, susceptible of a fine polish, and much used, both in ancient and modern times, as an ornamental stone. The colouration, which is distributed in bands or cloudy patches, is due to the presence of ferrous carbonate and ferric hydroxides, and to a less degree of manganese oxides and organic matter. For example, a green marble from Arizona contained 4.27 p.c.  $FeCO_3$ , and in its brownish-red (oxidised) portions 1.22 p.c.  $FeCO_3$  with 3.53 p.c.  $Fe_2O_3$ . The percentage of calcium carbonate rarely falls below 90. Onyx-marble is quarried in Algeria, Mexico, and Arizona. (See G. P. Merrill, The Onyx Marbles: their Origin, Composition, and Uses, both Ancient and Modern, Rep. U.S. Nat. Mus. for 1893, 1895, 539; G. P. Merrill, Stones for Building and Decoration, 3rd edit., New York, 1903). L. J. S.

**OOPHORIN** v. SYNTHETIC DRUGS.

**OPAL.** Colloidal silica, occurring native in botryoidal and stalactitic forms, or as irregular masses occupying cracks and cavities in certain rocks. It is softer and less dense than quartz; its hardness being only  $5\frac{1}{2}$  to  $6\frac{1}{2}$ , while its sp.gr. varies with the impurities present from 1.9 to 2.3. Being non-crystalline it should exhibit single refraction, but many varieties, especially of noble opal, are strongly birefringent; the anomaly being probably due to the strain set up by unequal contraction in different directions during the solidification of the gelatinous mass. Opaline silica is nearly always hydrated, but the proportion of water varies from about 2.5 to upwards of 10 p.c. Von Kobell found that the noble opal of Hungary lost 10.94 p.c. when strongly heated. The substance is almost wholly soluble in a hot solution of potassium hydroxide.

The purest opal, known as *hyalite* or *water-opal*, occurs as colourless, transparent masses, resembling glass. *Semi-opal* is a name applied to the dull, opaque varieties, generally more or less impure. *Menilite* or *liver-opal* is a brown

opaque mineral, occurring as nodules in the Tertiary strata of the Paris basin, especially at Menilmontant.

*Wood-opal* is simply wood fossilised with opaline silica, and retaining the ligneous structure, which produces a pleasing effect when the substance is cut and polished; hence it is used in slabs as an ornamental stone. *Hydrophane* is an opal which, when dry, is opaque and dead white, but absorbs water rapidly when moistened, becoming transparent and sometimes exhibiting a play of colours. A fine variety found in Colorado has been brought into use under the name of 'magic stone.'

*Common opal* is a general term for any opal which does not display sufficient colour to recommend it for use as a gemstone for decorative purposes.

Its appearance it often receives trivial names, such as milk-opal, wax-opal, &c. *Fire-opal*, found

exhibits a brilliant hyacinthine or orange colour, which renders it of some value in jewellery. But the finest variety of the opaline group of minerals is the *precious* or *noble opal*, a substance which is unique in exhibiting by reflected light a vivid play of iridescent colours. The cause of this phenomenon has been studied by Brewster, Crookes, Behrens, Lord Rayleigh, and others. By most authorities it has been referred to the presence of numerous microscopic pores, fissures, or striae in the interior of the stone; but Behrens considers it due to the interposition of thin lamellae of opaline matter having a different index of refraction from that of the matrix (Sitz.-Ber. Akad. Wiss. Wien. Math.-naturw. Cl. 1871, 61, 519). If the colours proceed from distinct patches, like a brilliant mosaic, the stone is termed in trade *harlequin opal*.

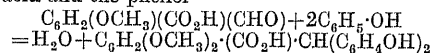
*Precious opal* is a mineral of very limited distribution. The oldest mines are those on the Dubnik Hill, near the village of Czerwenitz (Czerwenitz, Vátság), near Eperjes in Hungary, where the opal occurs in a matrix of sandstone. Slabs of matrix, or 'mother-of-opal,' enclosing brilliant particles of the gem, are polished as ornamental stones. Opal is also found at Gracías-a-Dios, in Honduras; at Queretaro, in Mexico; near the Barcoo river, and several other spots in southern and central Queensland; and at White Cliffs and other districts in northern New South Wales. The Queensland opal occurs in cracks in nodules of jaspery brown iron-ore, and is remarkable for its brilliant blue and green colours; that of White Cliffs, discovered in 1889, occurs in a white sandstone of Cretaceous age. Opals are usually cut *en cabochon*, i.e. with a convex surface, but the Queensland stone, occurring in thin layers, lends itself to cameo-work, the brown ferruginous matrix forming an effective background.

'Black opal,' enclosing patches of manganese oxide and exhibiting a brilliant play of colours, has recently been found at Lightning Ridge in northern New South Wales. In addition to the compact forms of opal mentioned above, there are also loose and friable forms of opaline silica represented by silicious sinter or geyserite (deposited by the hot springs of Iceland, New Zealand, and the Yellowstone Park in Wyoming) and by diatomaceous earth or kieselguhr (*q.v.*) (consisting of the silicious skeletons of diatoms and radiolaria).

L. J. S.

# OPHICALCITE v. MARBLE.

**OPIAURIN.** Opianic acid and phenol, when heated together with strong sulphuric acid, give rise to an intense yellow-red dye. The reaction takes place between the aldehyde group of the acid and the phenol



This compound is oxidised during the process to . . . . . The best results are obtained by stirring an intimate mixture of opianic acid and phenol into sulphuric acid (60°B.), and keeping the mixture well cooled. After 24 hours it is thrown into a large quantity of cold water, and the precipitate, when washed and dried, freed from tarry matters by extraction with hot benzene. Opiaurin is soluble in alcohol, ether, and glacial acetic acid, insoluble in benzene and light petroleum. It can only be obtained in the amorphous condition. It dissolves in alkalis with a purple colour; the solution in alcoholic ammonia becomes brownish-yellow on heating, but the purple colour returns on cooling.

Sulphurous acid does not reduce it. Opianic acid reacts in a similar way with other phenols, and the reaction can be used to detect the presence of opianic acid, as also of an aldehyde group in aromatic compounds; the reagents are separately dissolved in an excess of cold sulphuric acid; on mixing the solutions the colouration takes place at once (C. Liebermann and P. Seidler, Ber. 20, 873; J. Soc. Chem. Ind. 6, 541).

## OPIUM.

*Origin.*—Opium is the milky juice of the unripe capsules of *Papaver somniferum* (Linn.) or opium poppy, obtained by incision and inspissated by . . . . . The plant (*v. Benth.* a. . . . .) is indigenous to Asia Minor and neighbouring districts of South-Eastern Europe and Western Asia; but it is now cultivated more or less throughout all temperate and sub-tropical countries. It exhibits, however, morphological differences. The two most important varieties which, according to Boissier, are cultivated for the production of opium, are *glabrum*, with subglobular capsules and ten to twelve stigmata, and *album*, with egg-shaped capsules and without apertures (Flora Orientalis, 1867, 1, 116). The former is grown in Asia Minor and Egypt, and the latter in Persia and India. But besides these varieties there are minor distinctions, the petals in the same variety differ in colour, and may be white, red, or violet, with a dark-purplish spot at the base in most cases. The seeds are white or dark-coloured, and contain from a third to half of their weight of fixed oil. The capsules are provided with a lactiferous system from which the juice exudes when they are incised. This milky juice is present in the plant in all countries where it has been grown, and opium may be collected provided that the rainfall is not too great and the temperature neither arctic nor entirely tropical. That its production is confined for the most part to Asia Minor, Persia, India, and China, is determined by other considerations such as the value of land and the cost of labour.

*History.*—The drug was known early in the third century B.C. to Theophrastus. Scribonius

Largus, in the first century A.D., describes the method of preparing it and remarks that it should only be made from the capsules; for, as Dioscorides, writing a little later, points out, two sorts of opium were in use at that period. One of these, the opium proper, was prepared from the capsules, and the other, 'meconium,' was extracted from the entire plant by means of a solvent. Similar accounts may be found in the works of Pliny and other Latin writers. The opium of the classical period, and indeed the only variety known till the twelfth century, was exclusively that of Asia Minor. The nations of the East appear to have learned of opium from the Arabians, and it seems probable that the use of the drug was favoured by the Mahomedan prohibition of alcohol. They are supposed to have introduced the drug into China in the ninth century. Egyptian opium, 'Opium Thebaicum,' is mentioned by Simon Januensis about the end of the thirteenth century. At this time, and three centuries later, according to Prosper Alpinus, meconium was still prepared in the Thebaid in Upper Egypt.

In India opium was collected early in the sixteenth century. Barbosa describes a variety produced in Cambay. Pyres, the first European ambassador to China, writing in 1516, mentions three varieties of opium, obtained respectively from Egypt, Cambay, and from the kingdom of Cots. The last-mentioned district is Kus Behar, south-west of Bhotan in Bengal. Garcia d'Orta, a little later, remarks that Cambay opium is chiefly derived from Malwa. The opium production in India under the Moguls, of Clive at Plassy in 1757 the monopoly passed into the hands of the East India Company. The manufacture then greatly increased, and it has gone on increasing until within the last few years. It was during the seventeenth century that the first accounts reached us of the production of opium in Persia. Kämpfer found that the 'theriaka,' which had long been held in high esteem by neighbouring nations, was made by mixing the finer sorts of opium with spices.

The Chinese obtained their opium from India. Until the beginning of the eighteenth century it formed part of the return cargo of their junks. The importation was then small, and it was used almost exclusively in medicine as a remedy for dysentery. The imports did not reach 1,000 chests (Malwa chests contain one pecul, or 133½ lbs., Patna chests 160 lbs.) until 1767, when the trade was mostly in the hands of the Portuguese. In 1790, under the East India Company, it had become 4,054 chests. It was at this time that the habit of smoking began to spread in China. To promote the trade the East India Company established an opium dépôt of two ships, which lay off the island of Macao, at the entrance to the Canton river. The importation went on increasing, until in 1796 it was forbidden by the Chinese. In 1796, and that an edict was issued in 1820 prohibiting opium-laden ships from entering the river. The trade, which between 1820 and 1830 had risen to 7,000 chests annually, then assumed a contraband character. Complaints, however, continued, and when in 1839 it was decided to enforce the law, this, together with other difficulties, led to a war with England which terminated in the treaty of Nanking in 1842.

By this treaty five ports were opened to foreign trade, and the island of Hong Kong was ceded to the British Government. The export of opium from India into China, which in 1870 amounted to 55,000 chests, increased to 95,000 chests in 1880. Owing to Chinese home production, however, the importation of Indian opium then began to decrease until in 1890 it fell to 76,000 chests and in 1907 to 50,000. Recently, an important movement has arisen in China to put a stop to opium smoking throughout the Empire, and to this end to curtail both the home production and the importation from India. With regard to the Indian importation, the wish of China has been met by the Government of this country, and notwithstanding the serious loss which it entails to the revenue of India, which in 1880 amounted to Rs.8,500,000, and to the Indian poppy cultivators, the British Government, reciprocating the views expressed by the Chinese, entered into an agreement, the effect of which, it is hoped, will be that both the Chinese production and the Indian exportation to China will be made to decrease together, and that, according to well-informed opinion, will come to an end in a few years' time.

Numerous attempts had been made during the seventeenth and eighteenth centuries to prepare active condensed extractives from opium, but no constituent of a definite nature was discovered until the beginning of the present century. Derosne in 1803 noticed a separation of crystals on diluting an aqueous extract of opium (Ann. Chim. Phys. [i.] 45, 257). Their basic character was demonstrated by Robiquet in 1817 (*ibid.* [ii.] 5, 275), and the compound is now called *narcotine*. Derosne noticed that opium solutions are precipitated by alkalis, but thought that the precipitate was the same compound which he had previously isolated. Seguin in 1814 described what was probably the chief active constituent of opium (*ibid.* [i.] 92, 225), but to isolate in a definite form and make known the basic properties of *morphine* was reserved for Setürner, an apothecary of Einbeck in Hanover, whose work extended from 1805 to 1816. During the same inquiry, in 1806, Setürner also brought to light *meconic acid* with which the *morphine* is combined. *Morphine* was the first compound known belonging to the class of vegetable bases, which has since become so important; for although *narcotine* was isolated just before, its properties as an alkaloid were not ascertained until afterwards. Further historical and other details will be found in the article on opium in 'Pharmacographia' (Flick. a. Hanb. 272), from which many of the facts given have been obtained.

*Production.*—*Asia Minor.* Opium is collected in Asia Minor for the most part by small peasant proprietors, the largest quantity being obtained in those countries lying to the west, and having Smyrna and Constantinople for their ports of shipment. The product of these countries is the *Turkey* opium of English commerce, and of all available varieties it is the richest in *morphine*. The poppy grown is the variety *glabrum* of Boissier. The flowers are purplish or sometimes white, and the seeds white to deep violet. The plant grows

in elevated as well as lower situations, and requires a moist soil and much attention and skill on the part of the cultivator. Details of the mode of preparing the soil and management of the crop are given by Maltass (Pharm. J. [i.] 14, 395) and Heffler (*ibid.* [ii.] 10, 434), and in the official directions drawn up by the Turkish Government for the promotion of the opium culture in Macedonia (*ibid.* [iii.] 13, 918). The crop is sometimes destroyed by early frosts, drought, or the attack of locusts. The seed is sown from November to March, and the flowering takes place from May to July. In this way successive crops of capsules become ready for incision during a period of about three months, and a saving in the cost of labour is effected.

In the course of a few days, after the petals have fallen, when the capsules are some  $1\frac{1}{2}$  inches in diameter, they are ready for incision. This is done transversely around the middle by means of a knife. The operation is one requiring skill, for if the incision be not deep enough an incomplete flow of juice results, and if it be too deep some of the juice is lost inside the capsule. The incisions are made in the afternoon, and the exuded and partly hardened juice is collected the following morning. It is scraped off and placed on a poppy leaf. Masses of hardened juice thus obtained are allowed to stand in the shade to dry still further, and are then made into lumps of varying size and sold to dealers in the towns. By these the opium is manipulated into cakes suitable for the market, enveloped in poppy leaves and packed in bags, into which *Rumex* fruits are thrown to prevent the cakes adhering together. The bags are then sealed and transmitted to Smyrna and Constantinople, where they are received by the buyer, and the examiner scrutinises the drug piece by piece, and by its physical characters classifies it as (1) *prime*, (2) *current*, and (3) *chiginti*. The 'current' constitutes the great bulk of mercantile opium. An important addition to the profits of the opium culture is the sale of poppy seed, from which the oil is expressed and used for a variety of purposes. It is a bland, pale yellow oil, of a pale colour (Maltass; Pharm. J. [iii.] 11, 835).

Good Smyrna opium when dry contains 12 to 15 p.c. of morphine. If less than 10 p.c. is found in a specimen adulteration may be suspected. The opium used in medicine in this country when dried is required to contain not less than 9.5 and not more than 10.5 p.c. of morphine (Brit. Pharm. 1898). The dried Turkey opiums examined by Guibourt contained from 11.7 to 21.5 p.c. or a mean of 14.7 p.c. of morphine (J. 1862, 374). Of ninety-two specimens examined by Fayk Bey, the highest was 17.2 p.c., and half of them contained more than 10 p.c. (Plick. a. Hanb.). Bulgarian opium, analysed by Theegarten, gave:—Küstendil, in large lumps, 4 to 10 oz., 17.69 p.c.; Lowtscha, 11.90 p.c.; Halitz, 7.25 p.c. (Pharm. J. [iii.] 11, 896; 13, 342).

Turkey opium, as it appears in English commerce, consists of rounded masses, generally from  $\frac{1}{2}$  to 2 lbs. in weight but sometimes larger or smaller. Externally it is covered with poppy leaves and *Rumex* 'chaff.' It has a bitter taste, and peculiar, though not altogether dis-

agreeable, odour. The following are among the products of which the Constantinople market receives the opium of Macedonia and, until recently at least, small supplies from Bulgaria. The cultivation of opium in Macedonia commenced in 1865 from seeds brought from Karahissar. In 1882 the districts of Kotchava, Straumnitz, and Tikvish exported 135,000 lbs. by way of Salonica, whence it is termed collectively Salonica opium. The opium districts in Bulgaria are Küstendil, Lowtscha, and Halitz. The produce is mostly consumed by local pharmacy; but, while the country remained under Turkish dominion, any surplus found its way to Constantinople.

The Constantinople market receives the products of Afium Karahissar, Ushak, Akhissar, Tanshau, Isbarta, Koniyyeh, Bulladan, Hamid, Magnesia, and that collected in the neighbourhood which is known as Yerli.

In the English market, Turkey opium is divided into three classes, known as 'shipping,' 'druggists,' and 'manufacturing' opium. As shipping opium are classed those varieties which contain the least proportion insoluble in water, and which yield the greatest quantity of extract adapted for smoking. These are the opiums of Malatia, Tokat, Salonica, Balukhissar, Kurkagatsch, Bokaditz, and 'prime' Angora and Yerli. This opium is exported to China, Peru, the West Indies, British Guiana, Brazil, and for reshipment, to the United States. *Druggists'* opium is selected for a high percentage of morphine and includes the varieties which are used in medicine. It has a firmer consistence and a darker colour than the others. In England the products generally chosen are: Beybazar, Yerli, Karahissar, including Adet, Amasia, Akhissar, and 'current' Smyrna and Angora; for America, Ushak, Yerli, and Karahissar; and for the Continent, Ghéve. *Manufacturers'* opium is used for the preparation of alkaloids and includes 'chiginti,' Persian, and other low-priced opiums (Holmes).

Among the various adulterants which have been detected, from time to time, in Turkey opium are: sand, clay, grape-juice thickened with flour, fig-paste, liquorice, half-dried apricots, tragacanth, pounded poppy capsules, and even turpentine, stones, and bits of lead.

Of late years there has been a great decrease in the production of opium in Asiatic Turkey attributed entirely to the low prices.

*Egypt.* Only a small quantity of opium is now exported from Egypt. Owing to its inferior quality it is not regularly imported into England. Small consignments are, however, sent to Turkey and other countries on the Mediterranean sea-board. It is cultivated in Upper Egypt near Esneh, Kenneh, and Assiout, the ancient Thebaid. Allen, in 1861, describes the collection of opium from a white poppy. The capsules are slit twice transversely, and the juice collected the following day with a sort of scoop-knife, and placed on a leaf, in the sun, to harden (Pharm. J. [ii.] 4, 190). The product is sent out in cakes, enveloped in

poppy leaves, but without *Rumex* fruits. According to information given to Martindale, the best opium is produced at Akmin, on the right bank of the Nile, 320 miles above Cairo; while at Assiout, 250 miles above, an inferior quality is produced. A piece of Akmin opium, in the form of a hard flat cake, four inches in diameter, and one inch in thickness, contained 7.24 p.c. of morphine. There was the mark of a leaf adhering to it, and it had a rough and irregular appearance. A specimen from Assiout, consisting of segments of a cake, much softer and evidently adulterated, yielded only 0.6 p.c. of morphine (Pharm. J. [iii.] 19, 743). Other specimens have given 5.8 to 12.2 p.c. (Guibourt, J. 1862, 374), 3.4 to 3.9 p.c. (Petermann, J. 1866, 704), and 5.8 p.c., together with 8.7 p.c. of narcotine (Flück. a. Hanb.). It has also been shown by Gastinel that opium can be made in Egypt containing 11 to 12 p.c. of morphine. The fact that it generally contains only half that proportion is due partly to an over-moist soil and unskilful collection, but also doubtless to adulteration (Flück. a. Hanb.).

*Persia.* The quantity of opium produced in Persia has until recent years been small and inferior in quality. The *Terak-e Arabistan*, was the chief source, and Shuster, in Khuzistan. A good quality was produced near Sari and Balfarush, in Mazandaran, near the Caspian, and in the southern province of Kerman. Inferior sorts came from Shahabdulazim, Kashan, and Kum. The cultivation extends into Turkestan, where a sort of meconium is also manufactured. Part of these products went overland to China, by way of Bokhara, Khokan, and Kashgar, and another part found its way to Constantinople, by way of Trebizond, to be sold as Turkey opium (Flück. a. Hanb.). More attention is, however, now given to the cultivation of the plant and the collection of the juice, and there is less adulteration, the result being a great increase in the trade. The poppy cultivated is the variety *album* (Boissier), having roundish ovate capsules. Shiraz and Behbahan, the latter in the neighbourhood of Bushire, and other new districts, furnish supplies (Pharm. J. [iii.] 11, 804), and old centres like Kum, Teheran, and Yezd, have improved the quality of their product (*ibid.* [iii.] 15, 113, 430). Ispahan has now become the chief centre of the opium cultivation, the other important districts being Shiraz, Yezd, Khonsar, and also Khorasan, Kermanshah, and Fars.

About the year 1870 a regular export trade of Persian opium was established by water from the ports of Bushire and Bunder Abbas, in the Persian Gulf, and the quantity exported increased rapidly. By far the greater part is now sent by sea to the ports direct to Hong Kong, and the market with the product of the Malwa. A smaller part is shipped to the Straits Settlements, and the rest to England. A less important trade continues with Constantinople, by way of Trebizond and Samsun, and part of the opium made in Teheran, Tabriz, and Kermanshah, also finds its way to Smyrna.

In China, Persian opium has, to a certain extent, replaced Indian opium owing to its being manufactured to suit the Chinese taste. After it has been once smoked the residue in the

pipes, if the opium is of good quality, can be used mixed with fresh opium some six or seven times, whereas Benares opium cannot be used thus more than once. The smoke of the Persian opium is milder and in consequence more suitable to a tropical climate (J. Soc. Chem. Ind. 1892, 646). It is impossible to determine the opium production of Persia as no statistics are kept, but in the season 1905-1906, the value of the opium exported to different parts of the world was over £173,000.

The greatly increased consumption of opium in Persia has led to the extension of the cultivation of the poppy over the whole country.

The capsules are ready for cutting at the beginning of June. Since the lightest coloured opium commands the best price in the market, the incisions in the poppy heads are made at sunset and the exuded sap is collected before sunrise, as sunlight discolours the product. Vertical incisions are made, and the juice is collected and conveyed to the market in copper vessels. There it is manipulated to suit the tastes of buyers in Hong Kong and London, whither it is exported between September and January. One of the most celebrated products is that of the village of Kupa, a short distance east of Ispahan.

The opium for home consumption in Persia is prepared by adding 20 p.c. of foreign matter to the crude opium after its volume has been reduced one-sixth by evaporation. The added material is usually 'sarcocolla,' the resin of *Penae macronota* (Linn.), but sometimes a boiled extract of dried poppy heads, the seed of wild rue, and an extract obtained by steeping fresh poppy leaves in water, are added. The mixture is then boiled slowly for 3 hours with constant stirring, and the paste thus obtained is kneaded and rolled into small sticks for the market. The opium left in the pipes after smoking is prepared for further consumption by being mixed with about 10 p.c. of raw opium and is then smoked as *Terak-suchte* (burnt opium) or is eaten in the form of pills. The opium for export which is sold in lumps is prepared from the raw opium by drying until its bulk is reduced by about a quarter, and then adding from 50-70 p.c. of grape juice or other unknown ingredients. This opium is homogeneous and it does not present a granular appearance like the Turkish opium. Morphine in the good samples contains about 15 p.c. and the dry extracts contain about 18.5 p.c. of morphine (Siedler, Chem. Zeit. 26, 920; Stahl, *ibid.* 32, 804).

*India.* Opium is one of the most important products of India. It is a State monopoly of the Bengal Government in Behar and Benares, and is cultivated free in the Malwa and other districts of the native States, whence on arrival in British territory it pays duty.

The area devoted to poppy cultivation in Bengal comprises the large central tract of the Ganges, about six hundred miles in length and two hundred in breadth. It extends east and west, from Dinajpur to Agra, and north and south, from Gorakhpur to Hazaribagh. According to Watt, the average annual area actually occupied by the poppy in Bengal for the last thirty years has been 490,000 acres. The State does not restrict the cultivation of opium; but



it is a monopoly in the sense that what is cultivated must be sold to the Government at a price agreed upon beforehand. One object of these regulations is to prevent the neglect of cereals, for the poppy culture is very much more profitable; in Malwa it is said to realise from three to seven times as much as the ordinary crops. The opium of Behar and Benares is sold at auction in Calcutta, part is retained for consumption in India, but the greater portion is shipped to China.

The remainder of the opium raised in India is produced by the native States. The most important centre is the broad tableland of the Malwa and the adjoining slopes of the Vindhya Hills. The opening of the railway has given a great impetus to the cultivation in Rajputana and Malwa. Smaller quantities are produced in the Punjab, not only in the plains, but to the eastward of Lahore, in the valley of Bias, as high as 7500 feet above the sea. Kulu also produces excellent opium. It is raised in Nepal, Basahir, and Peshawar, at Doda Kashtwar, at the base of the Himalayas, in the Jammu territory, from which districts it is sent to China overland (Flück. a. Hanb.). Nearly all the opium produced in the native States, however, enters British territory, and pays a duty according as it comes from the districts of Ahmedabad, Ajmere, or Malwa. It is then sent to Bombay, whence, under the general name of Malwa opium, it is shipped to China.

The poppy grown in India is the same variety as that of Persia. The same requirements of soil and climate have to be met. In addition to the dangers to which the crop is exposed in Asia Minor the plant in India is liable to the attack of a parasitical species of broom rape, *Orobanche indica*, which attaches itself to the roots and causes the plant to wither. The factory for the Behar district is at Patna, and for the Benares district at Ghazipur, where the Government agents are stationed. In Benares and Behar the seed is sown in November, and the capsules are ready in February or March. They are then incised or scarified vertically, by means of an instrument called a 'nushtur,' constructed of several blades bound together (cf. plate, Pharm. J. [i.] 11, 207). This operation is repeated, in the course of a few days, on different sides, each capsule being scarified from two to six times. The next morning the juice, which has exuded, is scraped off by the use of a sort of concave trowel made of sheet iron, called a 'sectoah,' and collected in earthen pots. The poppy capsules are afterwards utilised in a variety of ways and the oil expressed from the seeds. In Malwa the capsules are ready in March or April. A somewhat different instrument is used to collect the juice, and from time to time this is dipped in linseed oil to prevent the juice adhering. Owing to the heavy dews the juice in India is much more moist than in Asia Minor (*ibid.* [i.] 11, 209).

When freshly collected the juice consists of a wet granular mass of a pinkish colour, from which there collects in the bottom of the vessel a dark coffee-coloured acid liquid 'pasewa' or 'pussewah.' More of this liquid is separated by draining, and the opium is then carefully dried by exposure to the air, but protected from

the rays of the sun. The drying is continued some three or four weeks until the moisture is reduced to 30 p.c., the amount allowed by the Government. In this state it arrives at the factory where it is examined and if satisfactory is packed. If great care is taken, by mixing low and high quality opiums, to send out a uniform product. It is manipulated into balls, and covered with poppy petals, which have been dried carefully. The petals are made to adhere together into a sort of shell by means of a liquid called 'lewa' or 'lewah,' made partly of opium and partly of 'pasewa.' The spherical cakes, which have a diameter of about six inches, and are not unlike in appearance a 24 lb. shot, are rolled in poppy 'trash,' powdered stalks, capsules, and leaves, put into earthenware moulds and exposed to the sun. If blisters form, the cake shells are opened, the gas allowed to escape and then tightly closed again. After three days, about the end of July, the cakes are put into frames and exposed to the air. There they remain, with constant watching, until October, when they are packed in chests, which contain wooden partitions into 40 cakes, and the interstices are filled with poppy 'trash.' The chests, which contain 160 lbs., are then ready for exportation to China (Batwell).

That which is consumed in India, 'abkari' opium, is prepared somewhat differently. It is dried by exposure to the sun until it contains only 10 p.c. of moisture, in which condition it admits of being moulded like wax. It is made into square bricks about 2 lbs. in weight, wrapped in paper and packed in boxes turn by turn in compartments. Except that the aroma is not quite so good, 'abkari' opium is equal in quality to that prepared for China (Batwell, Pharm. J. [i.] 11, 269, 306, 359).

The opium of Malwa and other native districts is not so uniform in quality as that of the Government factories. Malwa opium contains only about 5 p.c. of moisture, and it is sent out in bricks or rounded masses which are not incased in poppy petals.

The percentage of morphine in Indian opium is much less than that found in the opium of Asia Minor. It is remarkable that a superior product in this respect has not been obtained to supply the English market, especially in view of the decreasing trade between India and China. Benares opium in 1845-9 contained 2.2 to 3.2 p.c. of morphine (Batwell). Specimens of Patna garden opium, prepared especially for medicine, yielded 8.6 p.c. (Flück. a. Hanb.), 7.7 p.c. (Guibourt), 9.5 p.c. of hydrochloride (Christison). Specimens from the India Museum gave the following percentages of morphine: 'Khandesh,' 6.1 p.c.; 'medical opium,' 1852-3, part of a brick, 4.3 p.c.; 'garden Behar,' 4.6 p.c.; 'Abkari provision,' 'Patna,' 3.5 p.c.; 'Sind,' 3.8 p.c.; 'Hyderabad,' 3.2 p.c.; and 'Malwa,' 6.1 p.c. (Flück. a. Hanb.). Three specimens of Malwa opium examined by W. D. Howard contained 4.8 p.c., 6.0 p.c., and 9 p.c. of morphine (Flück. a. Hanb.).

Small quantities of morphine salts sometimes reach this country from India. They are made at the Government laboratories at Ghazipur from opium which has been confiscated on account of adulteration, and are not likely to



become an important article of commerce (J. Soc. Chem. Ind. 1889, 917).

*China.* The Chinese consume a good deal of the opium exported from India, Asia Minor, and Persia, but not so much as formerly owing to the enormous development of the production in China, and this quantity, in accordance with the policy of the Chinese Government, will become less and less until the use of opium for smoking is abandoned altogether. It is not possible to estimate the amount produced in China, but some idea of the enormous increase may be gathered from consular and other reports. The various attempts of the Chinese Government to prohibit the manufacture of opium have had little effect. It was about 1830 that it began to be produced in notable quantities. In 1869, in a Report on the Trade of Hankow, addressed to the . . . of customs at Peking, the annu . . . three provinces Yunnan, Kweichow, and Szechuen, was estimated at 41,000 peculs. In the same year it was reported that two-thirds of Szechuen and one-third of Yunnan was devoted to the poppy (Calcutta Blue Book, 205). In 1882 the annual production in the south-west of China, chiefly the provinces of Szechuen and Yunnan, was estimated at over 200,000 peculs, or more than twice the whole importation from India (Pharm. J. [iii.] 13, 225; cf. J. Soc. Chem. Ind. 1890, 74). In 1885 the imports of Indian opium in Manchuria had fallen to only 5 p.c. of what they were in 1866, its place being taken entirely by the native drug (Pharm. J. [iii.] 18, 280). In 1887 the district of Wenchow was occupied almost entirely in the production of opium. The country, viewed from a hill-top, was, in many places, one vast brilliant mass of poppy, with here and there a patch of green (J. Soc. Chem. Ind. 1888, 409). The consul at Niew Chang, in Manchuria, reports in 1889 that, although twenty years before 2,635 peculs of Indian opium supplied the whole province, at that time the port of Yingtzu alone consumed 3744 peculs annually. This enormous demand was being met almost entirely by the native drug.

Opium is cultivated chiefly in Szechuen, Yunnan, and Kweichow, to a less extent in Shanse, Shense, and Shantung, also in eastern Mongolia, and in Manchuria. The development of the poppy cultivation has been so great in many parts of China that it has seriously interfered with the supply of cereals. For this reason, since the famine, it has been prohibited in Shense, Honan, and Chihli. In Kwangtung the soil and climate are not suitable, and in Fuhkeen the production of sugar is equally or more remunerative (Holmes). In Szechuen, the poppy is a winter crop, and may be gathered in time to allow rice to be planted, and thus not interfere with the summer produce. The yield of opium is about 22 lbs. to the acre. Every part of the plant has a use, if only for manure, and thus the total return amounts to about double that of cereals. As soon as the summer crop is reaped, the soil is prepared and manured with night-soil. The seeds are sown in December, in drills  $1\frac{1}{2}$  foot apart, the white poppy being the most commonly cultivated in the low grounds. After a month, when the plants are a few inches high, the rows are thinned and banked up with earth. In March or April the

flowering takes place, and at this time the roots are again well manured with night-soil. The capsules are slit in April or May (Pharm. J. [iii.] 13, 225). According to Thorel, the scarification and collection is precisely the same as that carried on in India. Some Szechuen specimens seem to have been collected with the use of oil as in Malwa (Flück. a. Hanb.).

Yunnan and Szechuen opium is made into flat cakes and wrapped in white paper. It is darker and softer than that of Persia, which it resembles. Chekeang is a treacly extract sold in 2 to 4 lb. jars. The product of Shense was supposed to resemble in flavour the highly-prized Patna opium. Yunnan ranks next and then Szechuen (Holmes). A specimen of Chinese opium, examined by Jamieson, contained:—Moisture, 18 p.c.; morphine, 5.9 p.c. (or 7.2 p.c. in the dried drug); narcotine, 7.5 p.c.; ash, 7.5 p.c. (Report on Trade of Hankow). Authentic specimens examined by Sheppard gave the following percentages of morphine in the dried opium:—Szechuen, 2.2; Kweichow, 2.5; Yunnan, 4.1; Kansu, 5.1. Eatwell in Szechuen found 3.3 and in Kweichow 6.1. Sheppard found 5 to 14 p.c. of moisture and 36 to 53 p.c. of extract soluble in water (Flück. and Hanb.).

*Mozambique and Algeria.* In 1877 a Portuguese company was founded to commence the opium culture in Mozambique (Pharm. J. [iii.] 8, 1007; 10, 63, 13, 445). In 1882, according to Guyot, some three hundred labourers were employed . . . ambei opium between the Mt . . . rivers. The yield compares . . . that in India. The product is said to be largely admixed with foreign substances before being made into 500 gram balls, which are packed in boxes containing poppy 'trash,' and covered with indigenous cotton (Compt. rend. 95, 798). These balls are sometimes seen in the English market. According to more recent advices, the company has been obliged to go into liquidation, and the cultivation has been abandoned (Pharm. J. [iii.] 21, 87). Opium has been collected in Algeria in small quantity since 1828 (*ibid.* [i.] 15, 348). A dried specimen examined by Guibourt contained 12.1 p.c. of morphine (Jahrb. 1862, 374; Aubergier found 1.5 to 17.8 p.c. (Ann. Chim. Phys. [iii.] 20, 303).

*Australia.* The production of opium commenced about 1868, and the first specimen reached this country from Victoria, and was examined by Morson in 1869. It contained, according to Hood, 2 p.c. of morphine and 8 p.c. of narcotine (Pharm. J. [iii.] 1, 272). Specimens containing 4.2 to 7.1 p.c. of morphine were sent to England in 1870. They were produced in the village of Sunbury, near Melbourne (Hood). About this time the cultivation was commenced in Gippsland, and opium containing 9 p.c. of morphine, 4 p.c. of narcotine, and 6 p.c. of meconic acid, was obtained (Ward, *ibid.* [iii.] 1, 543). The Tuwoomba district in Queensland also furnished some good specimens (*ibid.* [iii.] 1, 972).

The chief part of colonial opium in the Melbourne market comes from the Bacchus Marsh district, where the cultivation has been carried on for years. The sowing takes place at three periods, about the first week in

May, the second or third week in June, and the latter part of July. By this means parts of the crop mature in succession. The average yield is 15 to 25 lbs. to the acre, but in a good season as much as 30 to 40 lbs. are obtained. In Europe the average yield to the acre is 25 lbs., and in India 30 to 40 lbs. When the capsules are ready, two incisions are made horizontally, half-way round, and the juice which exudes is collected the next morning. A few days later other incisions are made, until the capsule is exhausted. The opium is manipulated into balls and carefully dried. In quality it approximates to the product of Asia Minor. A specimen gave 11.5 of morphine from the dry drug. Another from Queensland contained 9.8 p.c. (Matthews, Austral. J. Pharm. Nov. 1887).

*Europe and North America.* Attempts have been made in most European countries, in Greece, Italy, Spain, France, Switzerland, Germany, England, and Sweden, to cultivate opium, and the results have shown that, providing the soil selected is suitable, and the rainfall not excessive, it is possible, in all these countries, to produce opium equal to that of Asia Minor. The most important European experiments have been conducted in France: A product called 'affium' has been made at Clermont-Ferrand, which is said to contain uniformly 10 p.c. of morphine; but it has not become an important article of trade (Flück. a. Hanb.; Auberger, Pharm. J. [iii.] 15, 693). Some interesting investigations have been made in the neighbourhood of Amiens, where specimens of dry opium were produced containing 16 and 20 and still higher percentages of morphine. It was observed that the morphine diminished when the juice was slowly dried, and the peculiar odour of the drug is ascribed to a species of fermentation (J. Pharm. Chim. [iv.] 6, 222). Guibourt found the percentage of morphine in French opium to vary from 12.1 to 22.8, the latter being the highest proportion of morphine ever recorded (*ibid.* [iii.] 41, 184, 201). Other analyses of French opium give 17.6 p.c. (Deschamps, Compt. rend. 40, 34); 17.5 (Chevallier, Flück. a. Hanb.); 8.2 (Roux, J. 1855, 717); 11.1 to 11.9 (Petermann, Jahrb. 1866, 704). German opium from Erfurt contained 16.6 and 20 p.c. (Biltz, Gm. 16, 415); from Wurtemberg, 12 to 15 p.c. (Hesse, Flück. a. Hanb.); and from Silesia, 9 to 10 p.c. (Hesse).

Experiments have been carried out on the cultivation of poppies for opium production in the gardens of the Pharmaceutical Institute of Berlin. The amount of opium from poppies in that latitude is satisfactory; but the cost of collecting it proves to be too high (Thoms, Zeitsch. angew. Chem. 21, 2208). The poppy is rarely grown in Russia, although there are many districts with a suitable soil and climate. Samples of Russian opium from the Semiret-schinsky district contained about 7.5 p.c. of morphine (Goldberg, Chem. Zeit. 25, Rep. 367).

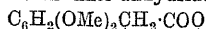
Experiments in North America lead to the same results as in Europe. Specimens from Vermont contained 15.75 p.c. of morphine (Procter, Amer. J. Pharm. [iii.] 18, 124); from

Illinois, 8.75 p.c. (Kennedy, *ibid.* [iv.] 1, 6); and from California, 7.75 p.c. (Maisch, *ibid.* [iv.] 3, 103).

**Chemical constituents.** The important chemical constituents of opium may be divided into alkaloids, neutral compounds, and acids. Of all of these see *VEGETO-*... are in opium some twenty alkaloids:—(1) *Morphine*,  $C_{17}H_{19}NO_3 \cdot H_2O$ , the most important constituent of opium. Its discovery and the proportion in which it occurs in opium have been already given. It is crystalline. (2) *Codeine*, morphine  $C_{18}H_{21}NO_3 \cdot H_2O$ , was discovered in opium by Robiquet (Annalen, 5, 106) and may be prepared by the action of methyl iodide on morphine. It melts at 155°. Percentage in Smyrna, French, or Indian opium, 0.2 to 0.4 (Pharm. J. [ii.] 7, 183). (3) *Hydrocotamine*  $C_{12}H_{15}NO_3 \cdot \frac{1}{2}H_2O$  occurs in small proportion in opium (Hesse, Annalen Suppl. 8, 326) and is formed by the oxidation of narcotine (Beckett and Wright, Chem. Soc. Trans. 28, 577). (4) *Thebaine*,  $C_{16}H_{21}NO_3$  was isolated by Thiboumery (Pelletier, J. Pharm. Chim. [ii.] 21, 569). Turkish opium contains about 1 p.c. (5) *Pseudomorphine*  $C_{34}H_{36}N_2O_8 \cdot 3H_2O$  (Pelletier and Thiboumery, *ibid.* [ii.] 21, 575) occurs in opium to the extent of 0.02 p.c. or even less. (6) *Codamine*,  $C_{20}H_{25}NO_4$ ; (7) *Laudanine*,  $C_{20}H_{25}NO_4$ ; (8) *Laudanosine*,  $C_{21}H_{27}NO_4$ , and (9) *Meconidine*,  $C_{21}H_{23}NO_4$ , which exist in opium in minute quantities, were discovered by Hesse (Annalen, 153, 47, 56; Suppl. 8, 272, 280, 321). (10) *Papaverine*,  $C_{20}H_{21}NO_4$ , was discovered by Merck in opium (Annalen, 66, 125; 73, 50). It exists to the extent of about 1 p.c. (11) *Lanthopine*,  $C_{32}H_{35}NO_4$  (Hesse, *ibid.* 153, 57; Suppl. 8, 271). (12) *Protopine*  $C_{20}H_{19}NO_5$  (Hesse, *ibid.* Suppl. 8, 318) and (13) *Cryptopine*,  $C_{21}H_{23}NO_5$  (T. and H. Smith, Pharm. J. [ii.] 8, 595, 716) are found in opium in very small proportions. (14) *Narcotine*,  $C_{22}H_{23}NO_7$ . The discovery of this base has been referred to already. It exists free in opium and may be extracted by benzene in which morphine is insoluble. Turkish opium usually contains 1 to 2 p.c., but East Indian and Persian opium often contain much more narcotine than morphine. In some specimens the proportion reaches 10 p.c. It is crystalline, melts at 176° and forms salts with difficulty. (15) *Nitropine*,  $C_{22}H_{23}NO_7$ , a base found in the *Papaver Rhoeas*, probably occurs in opium in minute quantity (Hesse, Annalen, 140, 145). (16) *Oxynarcotine*,  $C_{22}H_{23}NO_8$  (Beckett and Wright, Chem. Soc. Trans. 29, 461). (17) *Narceine*,  $C_{33}H_{37}NO_8 \cdot 3H_2O$ , was discovered by Pelletier in opium in which it is found to the extent of 0.02 to 0.1 or even 0.7 p.c. (Ann. Chim. Phys. [ii.] 1, 262). It consists of long colourless prisms which lose water at 100° and melt at 145° (Hesse, Ber. 7, 105). (18) *Gnoscopine* (*dl-narcotine*),  $C_{22}H_{23}NO_7$  (T. and H. Smith, Pharm. J. [iii.] 9, 82; 52, 794). (19) *Trilopine*,  $C_{42}H_{53}N_2O_7$  (Kauder, Arch. Pharm. 228, 419). (20) *Papaverosine*, a base found in poppy capsules by Deschamps (J. 1864, 446) but not hitherto detected in opium. (21) *Laudanidine*,  $C_{20}H_{25}NO_4$  (Hesse, Annalen, 282, 208). (22) *Xanthaline* or *Papaveraldine*,  $C_{20}H_{19}O_5N$  (T. and H. Smith, Pharm. J. 52, 793; Dobson and Perkin, Chem. Soc. Trans.

99, 135). (23) *Hydroxycodeme*,  $C_{15}H_{21}O_4N$  (Dobbie and Lauder, Chem. Soc. Proc. 1910, 339). With the exception of morphine and narcotine the remaining bases do not occur in opium to a greater extent together than 2 p.c. and generally not more than 1 p.c.

The neutral compounds are:—(1) *Meconin*,  $C_{10}H_{10}O_4$ , discovered by Dublanc (Ann. Chim. Phys. [iii.] 49, 5), but more completely studied by Couerbe (Annalen, 5, 180). It may be obtained by the oxidation of narcotine (Anderson, *ibid.* 86, 191; 98, 44) and is formed in other reactions. It is an inner anhydride



(Hessert, Ber. 11, 257). (2) *Meconoisin*,  $C_9H_{10}O_2$  or perhaps  $C_9H_2(Me)_2(OH)_2$ . It is crystalline, melts at  $88^\circ$ , and was found by T. and H. Smith in the mother-liquor from the reaction of meconin (Pharm. J. [iii.] 8, 981).

(3) *Meconic acid*,  $C_7H_4O_7 \cdot 3H_2O$  has already been mentioned. It is a tribasic acid forming primary, secondary, and tertiary salts.

It loses its water of crystallisation, and at  $120^\circ$  to  $200^\circ$  it breaks up into carbon dioxide and *comenic acid*  $C_6H_4O_6$ , and at a higher temperature into another molecule of carbon dioxide and *pyromeconic acid*,  $C_6H_4O_8$ . Meconic acid occurs in opium to the extent of 3 to 5 p.c. in combination with morphine, and perhaps with other bases. The 'bolactic acid' of T. and H. Smith (Pharm. J. [ii.] 7, 50) has been shown by Stenhouse (Watts' Dict. 1st ed. 5, 759) and Buchanan (Ber. 3, 182) to be identical with lactic acid. Turkish opium contains, according to T. and H. Smith, 2 p.c., but it is probably not an original constituent of the poppy-juice (Flück. a. Hanb.).

The less important constituents of opium represent three-fourths of its weight. *Water* exists to a very variable extent. Turkish opium contains on an average 12.5 p.c. The Bengal opium sent to China is made to contain uniformly 30 p.c. About 50 p.c. of opium is composed of a *gum*, having properties distinct from gum arabic, *pectin*, *albumen*, and fragments of capsules. *Sugar* is present in French opium to the extent of 6.5 to 8.0 p.c., and is said to be uncrystallisable. Of that part of Turkish opium insoluble in water, 6 to 10 p.c. is composed of *wax*, *pectin*, and insoluble calcium salts. The wax, which exists in the juice as an emulsion, is a mixture of *cerotyl palmitate*, and *cerotyl cerotate* (Hesse, Ber. 3, 637). Vermont opium contained 11 p.c. of *caoutchouc* (Procter). The *colouring matter* and a *pungent volatile substance*, which is removed by benzene or acetone, have not been examined. Opium leaves 4 to 8 p.c. of *ash* consisting chiefly of sulphate and phosphate of calcium and magnesium. Poppy-juice contains no starch or tannin. The presence of these substances in opium is therefore an indication of adulteration.

*Microscopic examination* of opium and the *extraction* by solvents (Deane and [ii.] 6, 234; 7, 183). Examples of analyses: Persian opium (W. D. Howard, *ibid.* [iii.] 6, 721); Australian opium (Ward, *ibid.* [iii.] 1, 543); J. Pharm. Nov. 1887); Vermont opium (Procter, Amer. J. Pharm. [iii.] 18, 124); Flückiger (Jahr. 1869, 797; Pharm. J. [ii.] 10, 208); Indian and Chinese

opium (Browne, *ibid.* 84, 452; van Itallie and Kerborsch, Arch. Pharm. 218, 609).

For determination of morphine in opium, v. Kobler (J. Soc. Chem. Ind. 14, 464); Dott (*ibid.* 15, 91); Gordin and Prescott (Arch. Pharm. 237, 380); Dowdard (Pharm. J. 71, 909); Schidrowitz (Analyst, 29, 144); and for determination of narcotine and codeine, van der Wielen (Pharm. Zeit. 48, 267); Caspara (J. Pharm. Chim. 20, 458); Andrews (Analyst, 36, 489).

*Physiological action and uses*.—Opium is without doubt the most important remedy available for use in medicine. Its action on man is chiefly on the brain, producing sleep. In doses of a grain or less, a stage of slight excitement supervenes during which the individual can control his energies. In 1 to 2 grain doses the stage of excitement is short and is succeeded by deep sleep, after which there is nausea and headache. If large doses of 3 grains or more be administered the excitement is very short and is followed by sleep which becomes more and more comatose until the patient cannot be aroused. If death takes place the respiration ceases first. Opium is used for the alleviation of pain, either generally or locally, for the production of sleep, or for reducing the irritation of various organs. Its special applications in the treatment of disease are almost endless (cf. Brunton, Pharm. Therapeut., 1887, 852).

The action of opium in stimulating and then depressing gives rise to the desire to repeat the dose. In this way the habit of 'opium eating' is contracted. The worst effects of opium are thus obtained. It deranges the nervous system, and impairs the intellectual and moral and finally also the physical powers. Dr Quincey's description of his own experience is well known.

But by far the largest quantity of opium is used for smoking. The habit is believed to have originated in Persia, but it is in China, where it prevails to the greatest extent at the present day, where, indeed, its use appears to be almost as widely diffused as the use of tobacco in Europe. For smoking the opium undergoes a process of preparation which is a business in itself. In Hong Kong, according to McCallum, the opium is extracted by boiling with water and the clear solution is evaporated until it attains the consistence of treacle (Pharm. J. [iii.] 11, 220; 12, 446). The Chinese in California first put the opium through a series of roasting processes which are said to destroy its stickiness and render it more easily extracted by boiling with water (Calvert, *ibid.* [iii.] 120, 148). The Chinese recognise four varieties of opium:—(1) Raw opium; (2) Prepared opium, the treacle extract described; (3) Opium 'dross', the scrapings of the opium pipe, which are said to be strong, hot, of inferior flavour; (4) Opium 'dirt', the exhausted marc after extraction with water (McCallum).

The whole operation of opium-smoking is described in a letter which accompanied an opium-smoker's set of apparatus in 1882 from Canton to Kew. The pipe has a flat bowl made of metal with a very small opening. A drop of the soft opium is taken on the point of a 'dipper' and dexterously roasted in the flame of a little lamp until with constant burning it has the appearance of burnt worsted. Then, first

warming the bowl of the pipe, the drug, about the size of a hemp-seed, is placed about the opening in the bowl, the pipe taken in the mouth and the opium ignited. The smoke is partly swallowed or inhaled and partly exhaled by the mouth and nose. The preparation for smoking occupies 5 or 10 minutes, but the actual smoking only about 30 seconds (Sampson, *ibid.* [iii.] 11, 22).

The physiological action of opium smoked in this way is clearly quite different from what it is when taken in the stomach. It is noteworthy that those opiums most highly prized for smoking contain a small percentage of morphine. It would seem that, notwithstanding the serious view of the effects of opium-smoking taken by the Chinese Government and held by many Europeans, the habit is not more injurious than the use of other stimulants. Opium in the East seems to perform the same function that alcohol does in the West, and, as far as can be ascertained, with about the same good and bad effects (*cf.* Birdwood, *Pharm. J.* [iii.] 12, 500; Spence, *ibid.* [iii.] 13, 226; McCallum, *ibid.* [iii.] 14, 27; James, *ibid.* [iii.] 18, 280).

A. S.

**OPOBALSAM** *v.* OLEO-RESINS.

**OPODELDOC.** *Linimentum Saponato-camphoratum.* A solution of soap, camphor, and volatile oils in alcohol, used externally in rheumatism, sprains, &c.

**OPOPANAX** or **OPOPONAX** *v.* GUM-RESINS.**ORANGE.** *Citrus Aurantium* (Linn.).

Many varieties are known, differing in size, shape, colour, flavour, and other respects. König gives a list of a very large number of

Mean wt. of fruit in grams.	Percentage proportion of—
	Rind    Flesh    Pips
188.4	27.8    71.0    1.2

The flesh contains—

	Water	Protein	Invert sugar	Cane sugar	Citric acid	Ash
	84.3	1.1	2.8	2.9	1.4	0.4

The juice contains—

	Total extract	Invert sugar	Cane sugar	Citric acid	Protein	Ash
	13.0	4.1	5.0	1.4	0.4	0.3

The following figures were obtained by Farnsteiner and Stüber (*Zeitsch. Nahr. Genussm.* 1904, 8, 603) from the examination of the juice of Valencia and Messina oranges:—

	Valencia oranges	Messina oranges
Sp.gr. at 15°	1.0464	1.0451
" " after boiling	1.0466	1.0455
Grams per 100 c.c.—		
Total solids, dried at 100°	10.92	10.85
Citric acid (anhydrous)	1.79	1.47
Total sugar (as invert sugar)	7.65	7.86
Ash	0.52	0.52
Nitrogen	0.099	0.075
Polarisation in 200 mm. tube, direct	-0.11°	+2.45
Polarisation in 200 mm. tube, after inversion	-3.16°	-3.66

The characteristic flavour of oranges is due to the sugar, free citric and malic acids, and essential oils which they contain. The last-mentioned is most abundant in the rind (*v.* OILS,

ESSENTIAL). The number of oranges consisting of glutamine (Scurti, 1908, ii. 16, 1370).

The fibrous, insoluble, inside portions of Japanese oranges were found to contain—

	Water	Protein	Fat	Galactan	Pentosan	Cellulose	Ash
	12.16	5.27	1.28	18.91	27.72	32.51	2.15

(Bahadur, *Bull. Coll. Agr. Tokyo Imp. Univ.* 1906, 7, 121). The leaves of the bitter orange (*Citrus vulgaris* [Risso]) contain stachydrine (Jahns, *Ber.* 1896, 29, 2065). Dried orange-peel, softened with acetic acid and boiled with water, yields about 8 or 9 p.c. of lavulose (Bauer, *Landw. Versuchs-stat.* 1894, 45, 298). H. I.

**ORANGITE.** An orange-coloured variety of the mineral thorite (*q.v.*), occurring as tetragonal crystals and irregular masses, occasionally a few ounces in weight, in the augite-syenite of southern Norway. It was described and named by C. Bergemann in 1851, and believed by him to contain a new element 'donarium.' The identity of the mineral with thorite has long been recognised.

L. J. S.]

**ORANGE, CHROME,** *v.* CHROMIUM.**ORANGE, CROCEIN** *v.* AZO-COLOURING MATTERS.**ORANGE FLOWERS, OIL OF,** *v.* OILS, ESSENTIAL.**ORANGE, GOLD** *v.* AZO-COLOURING MATTERS.**ORANGE LEAVES, OIL OF,** *v.* OILS, ESSENTIAL.**ORANGE M;** **ORANGE, MANDARIN;** **ORANGE, METHYL;** **ORANGE, NAPHTHOL,** *v.* AZO-COLOURING MATTERS.**ORANGE OCHRE.** *Burnt Roman ochre* *v.* PIGMENTS.**ORANGE OIL** *v.* OILS, ESSENTIAL.**ORANGE, PALATINE,** *v.* PALATINE ORANGE.**ORANGE RUSSET.** *Rubens madder* *v.* PIGMENTS.**ORANGE, SALICYLIC,** *v.* SALICYLIC ACID.**ORANGE YELLOW** *v.* AZO-COLOURING MATTERS.**ORCEIN** *v.* Orcinol, art. PHENOL AND ITS HOMOLOGUES.**ORCHELLA WEED** *v.* ARCHIL.**ORCHIDIN** *v.* SYNTHETIC DRUGS.**ORCHIL** *v.* ARCHIL.**ORCHIL SUBSTITUTE** *v.* AZO-COLOURING MATTERS.**ORCHIPIN** *v.* SYNTHETIC DRUGS.**ORCIN** *v.* Orcinol, art. PHENOL AND ITS HOMOLOGUES.**ORCINOL** *v.* PHENOL AND ITS HOMOLOGUES.

**ORDEAL BEAN.** *Calabar Bean, Physostigma, Eséré Nut (Fève de Calabar, Fr.; Kalabarbohne, Ger.).* The seeds of the *Physostigma venenosum* (Balfour), a climbing plant, inhabiting the banks of the Niger and Old Calabar rivers near their mouths, in Western Africa (*cf.* Benth. *a. Trim.* 80, and, for an allied species, Holmes, *Pharm. J.* [iii.] 9, 912). The plant has a woody stem, and ascends to a height of fifty feet. The seeds are exceedingly poisonous, known to the natives in the Gulf of Guinea, by whom they are used as an ordeal to be undergone in cases of suspected witchcraft. Daniel, about 1840, introduced ordeal bean into

Europe (N. Ed. Pharm. J. 40, 373). The physiological action was examined by (Pharm. J. 14, 470). It causes a marked contraction of the pupil of the eye, and on this account is much used in ophthalmic medicine. With regard to the antagonism between ordeal bean and belladonna, v. Bennett (Brit. Med. J. 1875, 464). It is given in cases of poisoning by strychnine, and generally in tetanus and chorea (cf. Flück. a. Hanb. 191).

The physiological activity of ordeal bean depends chiefly upon the presence of the alkaloid *physostigmine* or *eserine*,  $C_{15}H_{21}N_3O_3$ , discovered by Jobst and Hesse (Annalen, 129, 115). To obtain it, the seed is exhausted with alcohol, and the alcohol removed from the solution by distillation. The residue is mixed with sodium bicarbonate and extracted with ether. The ethereal solution is shaken with water containing sulphuric acid, and the acid solution of alkaloidal sulphate is treated with excess of sodium bicarbonate. Ether now extracts the *physostigmine* and yields it as a brittle varnish on evaporation (Hesse, Annalen, 139, 82). Petit shakes the last ethereal solution with water, containing just sufficient sulphuric acid to neutralise the alkaloid. In this way, after removal of the ether and evaporation, crystals are obtained of neutral sulphate of *physostigmine* (J. Pharm. Chim. [iv.] 14, 255).

*Physostigmine* is tasteless but exceedingly poisonous. It forms colourless or pinkish crystals which melt at  $105^{\circ}$ – $106^{\circ}$  (Petit and Polonowsky, J. Pharm. Chim. [v.] 29, 55). It is soluble in alcohol, ether, benzene, carbon disulphide, and chloroform; but is only sparingly soluble in water. It oxidises readily, especially when moist, at  $100^{\circ}$ , a compound being formed

which gives a red colour with acids. It is precipitated by ferric chloride, and combines with acids to form salts. Most alkaloidal reagents precipitate *physostigmine*. The compound with potassium-mercuric iodide  $C_{15}H_{21}N_3O_3 \cdot KI \cdot HgI_2$  is white, insoluble in water, but soluble in alcohol, from which it may be obtained in crystals which melt at  $70^{\circ}$  (Hesse). When the alkaloid is neutralised with dilute sulphuric acid, an excess of ammonia added, and the mixture evaporated to dryness, a magnificent blue residue remains. The blue compound is soluble in water and alcohol, and may be crystallised from these solvents in elongated prisms. If to a solution of the base in water ammonia be added and the mixture be evaporated at  $100^{\circ}$  a bluish residue remains, which on the addition of an acid becomes beautifully dichroic blue and red (Petit, Compt. rend. 72, 569; J. C. Umney, Pharm. J. [iii.] 20, 1061). When heated with aqueous alkalis in presence of air, *eserine* first yields *rubreserine*,  $C_{15}H_{19}N_3O_2$ , which crystallises in red needles, but which is gradually converted into *eserine blue*. This is a true dye, colouring silk and wool without mordants (Ehrenburg, Chem. Zentr. 1894, ii. 439). A list of colour reactions of *eserine* is given by Reichard (Pharm. Zentr. 50, 375).

According to Harnack and Witkowsky (Pharm. J. [iii.] 8, 2), ordeal bean contains a second alkaloid, *calabarine*, which differs in its solubilities and its physiological action from

*physostigmine*; indeed, it appears in the latter respect to resemble strychnine. Another compound, *phytosterol*, has been isolated by Hesse (Annalen, 192, 175). It consists of brilliant tabular crystals, which melt at  $132^{\circ}$ – $133^{\circ}$ , and is extracted from the seed by light petroleum (cf. MacEwan, Pharm. J. [iii.] 17, 641). Windaus and Hauth (Ber. 39, 3478) show that this product is not a single substance. By suitable treatment it can be separated into *sitosterol*  $C_{27}H_{46}O$ , m.p.  $136^{\circ}$ – $137^{\circ}$ , identical with the compound obtained from ergosterol (Monatsh. 1900, 31, 100), m.p.  $170^{\circ}$ . By acting on *physostigmine* with reducing agents, Eber (Pharm. J. [iii.] 19, 161, 345) has obtained a compound *eseridine*  $C_{15}H_{23}N_3O_3$ , which is said also to be a constituent of the seed (Böhringer und Söhne, Pharm. Post, 21, 663). It liberates iodine from hydriodic acid. By treatment with acids it is reconvertible into *physostigmine*. *Eseridine* is distinguished from *eserine* by not yielding rubreserine under the influence of alkalis and air. A further alkaloid has been isolated by Ehrenberg (l.c.), *eseramine*  $C_{16}H_{25}N_3O_3$ , which crystallises from alcohol in slender white needles. It is not identical with Harnack's calabarine and doubts are expressed whether calabarine exists as such in the beans. Ogui (Apoth. Zeit. 19, 981) has also described another alkaloid, *isophysostigmine*, isomeric with *physostigmine*, but Salway (Chem. Soc. Trans. 99, 2148) obtained no evidence of the presence of this alkaloid or of *eseridine*. Salway finds that *physostigmine* can be obtained in two interconvertible modifications, m.p.  $86^{\circ}$ – $87^{\circ}$  and  $105^{\circ}$ – $106^{\circ}$  respectively, and he has also isolated a new alkaloid, *physoverine*  $C_{14}H_{15}O_3N_2$ , m.p.  $123^{\circ}$ , which, like *physostigmine*, produces a powerful myotic effect on the pupil of the eye, in addition to *calabarol*  $C_{23}H_{36}O_4$ , m.p.  $245^{\circ}$ , a new dihydric alcohol, and *trifolanol*  $C_{21}H_{36}O_4$ , a dihydric alcohol previously isolated from red clover flowers.

For estimation of alkaloids in ordeal bean by means of Mayer's reagent v. Masing (Arch. Pharm. 1877, 310). Gravimetric methods (Gibson, Pharm. J. [iii.] 15, 593; MacEwan, *ibid.* [iii.] 15, 594; 17, 642).

**OREIDE.** An alloy of a brilliant-yellow colour, resembling gold, made by taking copper 100, zinc 17, magnesia 6, sal ammoniac 3.6, lime 1.80, and tartar 9. The copper is melted and the other materials are added in small portions at a time, and the fused mass is skimmed and kept melted for about half an hour. The alloy has a fine grain, is malleable, takes a most brilliant polish, and if it tarnishes its lustre is restored by acidulated water.

**ORELLIN.** A yellow colouring matter contained in annatto, which is derived from the fruit capsules of *Bixa Orellana* (Linn.). Soluble in water and alcohol.

**ORICHALCUM.** A form of brass in use among the ancient Greeks and Romans.

**ORIENTAL EMERALD, ORIENTAL TOPAZ v. CORUNDUM.**

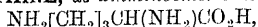
**ORIENTAL ALABASTER v. ONYX-MARBLE.**

**ORIGANUM OIL v. OILS, ESSENTIAL.**

**ORIOLE YELLOW v. PRIMULINE AND ITS DERIVATIVES.**

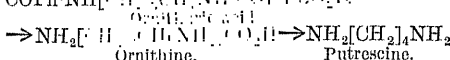
**ORMOLU v. MOSAIC GOLD.**

**ORNITHINE**,  $\alpha\delta$ -diaminovaleric acid



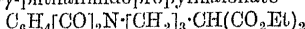
was first prepared by Jaffé (Ber. 1877, 10, 1926; 1878, 11, 40) from its dibenzoyl derivative *ornithuric acid*, found in the excrement of birds that had been fed with benzoic acid. It occurs among the products of alkali hydrolysis of certain proteins, probably arising from arginine by a further hydrolysis (Kossel and Weiss, Zeitsch. physiol. Chem. 1909, 59, 492; 60, 311; 1910, 68, 160); and it can also be obtained from arginine by the action of *arginase* (*q.v.*); or by hydrolysis with barium (Kossel, Ber. 1907, 40, 1926) and Winterstein, Ber. 1897, 30, 1926).

Jaffé (*loc.*) showed that ornithine was a diaminovaleric acid, the position of the two amino groups being determined by Ellinger (Ber. 1898, 31, 3183), who obtained *putrescine* (tetramethylenediamine, Udransky and Baumann, *ibid.* 1888, 21, 2938) and carbon dioxide by the action of fuming-sulphuric acid on ornithine.



Ornithine has been synthesised by Fischer (Ber. 1901, 24, 454) by the following series of reactions:—

Ethyl- $\gamma$ -phthalimidopropylmalonate

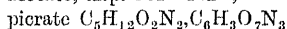
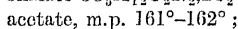
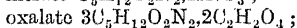
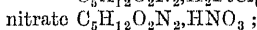
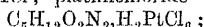


obtained from potassium phthalimide, propylene bromide, and ethyl sodiomalonate, yields ethyl  $\alpha$ -bromoisovaleric acid,  $\text{C}_4\text{H}_7\text{BrO}_2$ , with loss of carbon dioxide into  $\alpha$ -bromoisovaleric acid  $\text{C}_4\text{H}_7[\text{CO}_2]\text{N}[\text{CH}_2]_3\text{CHBr}(\text{CO}_2\text{H})$ , which, on treatment with ammonia and subsequent hydrolysis, yields  $\alpha$ , $\delta$ -diaminovaleric acid or inactive ornithine. A similar synthesis has been effected by Sørensen (Zeitsch. physiol. Chem. 1905, 44, 448); and a synthesis from benzoylpiperidine is described by Fischer and Zemlin (Ber. 1909, 42, 1022).

Ornithine is not crystalline, but forms crystalline salts; it is readily soluble in water, forming an alkaline solution; it contains an asymmetric carbon atom and derivatives of the dextro, levo, and racemic varieties are described.

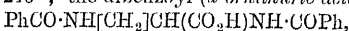
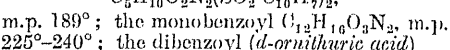
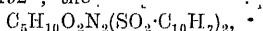
***d*-Ornithine.** The ornithine hydrochloride obtained by hydrolysis of naturally occurring ornithuric acid has  $[\alpha]_D +15.64^\circ$  to  $16.8^\circ$  (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1901, 34, 128), and *d*-ornithine is also obtained by the hydrolysis of *d*-arginine with barium hydroxide.

**Salts.** Hydrochlorides  $C_5H_{12}O_2N_2 \cdot 2HCl$  and  $C_5H_{12}O_2N_2 \cdot HCl$ ; platinichloride

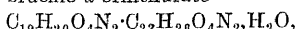


(Schulze and Winterstein); or with  $1\text{H}_2\text{O}$ , m.p.  $198^\circ\text{--}199^\circ$  (Riesser); or m.p.  $203^\circ\text{--}204^\circ$  (Kossel and Weiss).

*Acyl derivatives.*  $\text{C}_{10}\text{H}_{17}\text{NO}_2$ , m.p.  $191^\circ\text{--}192^\circ$ ; the



m.p. 184°-185°,  $[\alpha]_D +9.2^\circ$  to  $9.3^\circ$  in 10 p.c. solution of sodium salt,  $+8.5^\circ$  in 20 p.c. solution; brucine *d*-ornithurate

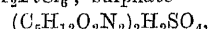


m.p. 135°–136°, separates from a solution of brucine in racemic ornithuric acid.

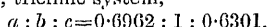
**L-Ornithine. Acyl derivatives.** The dibenzoyl (*L*-ornithuric acid)  $C_{19}H_{20}O_4N_2$ , from *dl*-ornithuric acid by fractionation, m.p.  $154^{\circ}-155^{\circ}$  of the cinchonine salt; m.p.  $189^{\circ}-190^{\circ}$  in 10 p.c. solution of the sodium salt; cinchonine *L*-ornithurate  $C_{19}H_{20}O_4N_2 \cdot C_{19}H_{22}ON_2 \cdot H_2O$ , the anhydrous salt has m.p.  $154^{\circ}-155^{\circ}$  (corr.); monobenzoyl  $C_{12}H_{16}O_3N_2$ , m.p.  $240^{\circ}$ ; the phenylisocyanate, m.p.  $189^{\circ}-190^{\circ}$  (corr.); the hydantoin, m.p.  $191^{\circ}$  (corr.).

*dl*-**Ornithine**, obtained by the putrefactive hydrolysis of arginine carbonate (Ackermann, *Zeitsch. physiol. Chem.* 1908, 56, 305); by hydrolysis of clupeine sulphate with barium hydroxide (Kossel and Weiss, *ibid.* 1909, 59, 492; 60, 311); is also prepared by any of the synthetic methods described above.

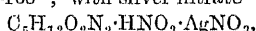
**Salts.** Hydrochloride  $C_5H_{12}O_2N_2.HCl$ , m.p.  $215^\circ$ ; aurichloride  $(C_5H_{12}O_2N_2)AuCl_4$ ; does decompose at  $215^\circ$ ; do  $C_5H_{12}O_2N_2.H_2PtCl_6$ ; sulphate



m.p. 213°; nitrate  $C_6H_{11}O_2N_2 \cdot HNO_3$ , m.p. 183°; oxalate  $C_6H_{11}O_2N_2 \cdot C_2H_2O_4$ , m.p. 218°; carbonate; acetate  $C_6H_{11}O_2N_2 \cdot C_2H_3O_2$ , m.p. 163°–164°; monopericate  $C_6H_{12}O_2N_2 \cdot C_6H_3O_7N_3$ , m.p. 170° triclinic system.

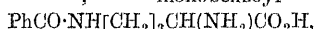


$\alpha=93^\circ 10'$ ,  $\beta=100^\circ 55'$ ,  $\gamma=81^\circ 19'$ ; dipicrate,  $C_5H_{12}O_2N_2 \cdot (C_6H_3O_4N_3)_2 \cdot 2\frac{1}{2}H_2O$ , m.p.  $183^\circ-184^\circ$ ; picronolone  $C_5H_{12}O_2N_2 \cdot C_6H_3O_4N_3 \cdot H_2O$ , m.p.  $220^\circ-221^\circ$ . Double salt. phate  
( $C_5H_{12}O_2N_2$ ) $\cdot CuSO_4 \cdot H_2O$ , m.p.  $204^\circ-205^\circ$ ; with cupric nitrate ( $C_5H_{12}O_2N_2$ ) $\cdot Cu(NO_3)_2 \cdot \frac{1}{2}H_2O$ , m.p.  $167^\circ-168^\circ$ ; with silver nitrate

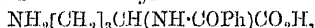


m.p. 175°.

*Acyl derivatives.* The phenylisocyanate, m.p. 192°; the hydantoin, m.p. 194°-195°; the monobenzoyl, C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N<sub>2</sub>(C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>), m.p. 180°.



m.p. 260°, or 285°–288° on the Maquenne block; the  $\delta$ -*m*-nitrobenzoyl  $C_{12}H_{15}O_5N_3$ , m.p. 250°; the  $\alpha$ -monobenzoyl



m.p. 264°-267°, on the Maquenne block; and (dl-ornithuric acid)  $C_{19}H_{20}O_4N_2$ , M. A. W.

**ORPHOL.** Bismuth  $\beta$ -naphtholate, *v.* BISMUTH, ORGANIC COMPOUNDS OF; *also* SYNTHETIC DRUGS.

**ORPIMENT** (*Auripigmentum*). Native arsenic trisulphide,  $As_2S_3$ , crystallising in the orthorhombic system and isomorphous with stibnite ( $Sb_2S_3$ ). Crystals are rare, the mineral usually occurring in laminated or scaly masses with a cleavage parallel to the surface of the plates. The colour is lemon-yellow, and there is a pearly lustre on the cleavage surfaces. The mineral is very soft and sectile (H. 1½-2), and the flakes are readily bent; sp.gr. 3.48. Orpiment occurs, usually in association with

realgar (*q.v.*), in mineral-veins together with ores of silver, lead, &c., and also as nodules in beds of sandy clay. It is found at several places in Hungary, at Mercur in Utah, and in some abundance at Julamerk in Asiatic Turkey. Some hundreds of tons are exported annually from Shih-haung-Ch'ang in prov. Yunnan, China. The mineral is used as a pigment (King's yellow), but now mostly in the East; it is the auripigmentum (golden paint) of the ancients. Formerly it was also used in dyeing and calico-printing, and by tanners for removing hair from skins. L. J. S.

**ORRIS ROOT** is the peeled and dried rhizomes of *Iris florentina* (Linn.), *I. pallida* (Lam.), and *I. germanica* (Linn.). It is characterised by a pleasant aroma, and appears to be slightly detergent. Formerly it was employed in the preparation of perfumes and dentifrices, and to a small extent as an ingredient of snuff.

#### ORSELLINE *v.* AZO-COLOURING MATTERS.

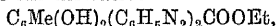
**ORSELLINIC ACID**,  $C_8H_8O_4 \cdot H_2O$ , was first prepared by Stenhouse (Annalen, 68, 61), by digesting lecanoric acid with boiling baryta water, and can also be produced from erythrin in a similar manner. According to Hesse (*ibid.* 139, 35), the solution of erythrin in baryta water is heated on the steam bath until a sample of the product no longer yields a gelatinous precipitate when neutralised with hydrochloric acid. The liquid is then acidified, and the orsellinic acid, which separates on standing, is crystallised from alcohol or acetic acid.

Orsellinic acid crystallises from dilute acetic acid in needles with  $1H_2O$ . When heated, it melts at  $176^\circ$  with evolution of carbon dioxide and formation of orcin, and is evidently an orcin carboxylic acid.

*Ethyl orsellinate*  $C_{10}H_{12}O_4$ , colourless leaflets, m.p.  $132^\circ$ , is produced when erythrin is boiled for several hours with alcohol (Stenhouse, *l.c.*), and can be prepared in an identical manner from lecanoric acid (Schunck, Annalen, 54, 265).

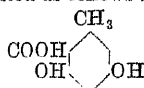
*Methyl orsellinate*  $C_9H_{10}O_4$  (Schunck, *l.c.*, and Stenhouse, *l.c.*), and *isomethyl orsellinate*  $C_{11}H_{12}O_4$  (Stenhouse; Hesse, Annalen, 139, 37), m.p.  $76^\circ$  have also been obtained.

According to Henrich (Ber. 1904, 37, 1406), ethyl orsellinate in alkaline solution reacts with diazobenzene chloride, with formation of the disazobenzene derivative



red needles, m.p.  $186^\circ$ , and this, on reduction with stannous chloride and hydrochloric acid, and further heating with hydrochloric acid at  $160^\circ$  gives diamino-orcin hydrochloride

$C_6HMe(OH)_2(NH_2)_2(Me:(NH_2)_2:(OH)_2=1:2:4:3:5$ . The constitution of orsellinic acid is therefore to be represented as follows:—



A. G. P.

**ORTHITE**, or Allantite. A complex rare-earth silicate belonging to the epidote group of minerals, and sometimes known as cerium-epidote. The general formula is  $YR''R_3Si_2O_{12}$ , where  $R''=Ca, Fe$ , and  $R'=Al, Fe, Ce, La, Di, Y$ . The extreme values in the analyses

tabulated by Dana are:  $SiO_2$ , 29.3-34.5;  $ThO_2$ , trace-3.5;  $Al_2O_3$ , 6.3-22.9;  $Fe_2O_3$ , 1.6-21.2;  $Ce_2O_3$ , 1.3-33.7;  $Di_2O_3$ , 2.9-24.0;  $La_2O_3$ , 0.2-8.1;  $Y_2O_3$ , 0.3-4.2;  $Er_2O_3$ , 0-2.0;  $H_2O$ , 0.3-14.6; also small amounts of manganese oxide, magnesia, and alkalis. Sp.gr. 3.5-4.2. The mineral crystallises in the monoclinic system, and has either a tabular or a long-prismatic habit. Compact masses and grains are also common. It is black or dark brown, opaque, and with a pitchy lustre on the bright sub-conchoidal fracture. On the exterior the material often presents a dull weathered appearance, the slender prismatic crystals looking rather like rusty nails. Tabular crystals from Greenland were described by T. Allan in 1808, and named allanite by T. Thomson in 1810. The later name orthite (from *orthos*, straight) was given by J. J. Berzelius in 1818 to long prismatic crystals from Finbo in Sweden. Owing to difficulties of determination and to differences in composition and degree of hydration, several other minerals, now recognised as varieties of allanite, have been described as distinct species under special names. As an accessory constituent of crystalline rocks (gneiss, granite, andesite, &c.), allanite is not of uncommon occurrence in small amounts. It is well known in the granite at Criffel and several other places in Scotland, and in a quartz vein traversing granophyre in Merionethshire. It is found in some abundance in the felspar quarries of Sweden and Norway, and as large masses in gneiss at several American localities. Masses weighing over 300 pounds have been found at Barringer Hill in Llano Co., Texas, where, together with gadolinite, &c., it has been quarried for the supply of rare earths used in incandescent gas-lighting. L. J. S.

#### ORTHOCLASE. *Potash felspar v. FELSPAR.*

#### ORTHOFORM *v.* SALICYLIC ACID.

**ORTOL**. Trade name for a mixture of methyl-o-amidophenol and hydroquinone. Used as a photographic developer.

**OSAZONES**. A term given by E. Fischer to compounds of phenyl hydrazine with the sugars (*v.* HYDRAZONES and CARBOHYDRATES).

#### OSMIRIDIUM *v.* PLATINUM METALS.

**OSMITOPSIS**, OIL OF. *Osmitopsis asteriscoides* (Cass.), an aromatic plant of the order of *Compositae*, growing in South Africa, yields a greenish-yellow oil of a burning taste and aromatic smell. Appears to be isomeric with borneol and oil of cajeput.

#### OSMIUM. Sym. Os. At.wt. 190.9.

This metal occurs in native platinum (*v.* PLATINUM), and especially in osmiridium. It differs from the other metals of the platinum group in forming a volatile tetroxide  $OsO_4$ , upon the production of which the separation of osmium from the other platinum metals, and especially from ruthenium, depends.

The osmiridium treated as described under Iridium (*v.* also *infra*) yields the osmium in the form of this tetroxide, which may be reduced in hydrochloric acid solution by zinc or mercury (Berzelius, Ann. Chim. Phys. 1829, [ii.] 40, 258); with an alkaline formate; with hydrogen; a mixture of carbon monoxide and dioxides or with carbon. In the latter case, the metal is obtained in a crystalline form, whilst by the other methods it is precipitated as a bluish

powder (Doebereiner, *Annalen*, 1835, 14, 17; Deville and Debray, *Compt. rend.* 1876, 82, 1077).

The metal has also been obtained by the reduction of its ammoniacal or sulphur compounds (Berzelius, *l.c.*; 1829, [iii.] 42, 191; Fromy, *ibid.* 1855, [iii.] 44, 387; Schneider, *Annalen*, 1867, Suppl. 5, 261).

Osmium has a sp.gr. of 22.48 (Joly) (its sp.gr., however, depends on its state of division); and melts at between 2300° and 2500°. It volatilises in the electric furnace, but less readily than the other platinum metals, so that it possesses special interest as being the least fusible and probably the least volatile metal and as the heaviest known substance, qualities which, in conjunction with its oxidation, and the peculiar nature of its oxide, distinguish it from the other platinum metals or indeed from all other known metals.

When heated osmium combines directly with fluorine, chlorine, sulphur, and with phosphorus. It is not attacked by hydrochloric acid unless the latter contains oxygen (Matignon, *Compt. rend.* 1903, 137, 1051).

Although osmium, when obtained in a finely divided state by treatment of an alloy with a solvent which removes the other metal, is easily oxidised or dissolved, it is much more refractory after ignition in an inert atmosphere, and is best rendered soluble by fusion with peroxides or with a mixture of caustic alkali and nitre.

On account of its infusibility, it has been employed for the manufacture of electric-light filaments, but by reason of its high cost and the extremely small supply, its use has been abandoned in favour of tantalum filaments or of the 'osram' filaments, which are made of tungsten wire and do not contain osmium as the name might imply.

It is stated by W. C. Heraeus, that 1 part of osmium will replace 2½ parts of iridium for hardening platinum, and that the improvement in elasticity is still greater. From 1 to 20 p.c. of osmium is recommended, the alloy being made in the absence of oxidising gases, and the presence of iron and copper being carefully avoided. The alloy has been patented (Eng. Pat. 29723, 1910).

None of the osmium compounds is of technological interest, excepting the tetroxide and the osmates, as forming steps in the preparation of the metal, and (as pointed out on account of a limited use) as staining pathological specimens. Colloidal osmium has been obtained by the reduction of its salts with hydrazine hydrate (Castoro, *Zeitsch. anorg. Chem.* 1904, 41, 131; Gutbier and Hofmeier, *J. pr. Chem.* 1905, [ii.] 71, 452).

#### COMPOUNDS OF OSMIUM.

**Oxides.** Osmium monoxide OsO is a greyish-black powder formed when the corresponding sulphite is ignited with sodium carbonate in a current of carbon dioxide.

Osmium sesquioxide Os<sub>2</sub>O<sub>3</sub> is obtained similarly as a black powder, or in copper-red scales by the reduction of the tetroxide. A corresponding brownish-red hydroxide is precipitated by the addition of alkalis to alkali osmochlorides.

Osmium dioxide OsO<sub>2</sub> is obtained similarly, and like the foregoing oxides, is feebly basic. It is bluish-black, but when prepared by heating its hydroxide in a current of carbon dioxide, it forms masses having a copper lustre. In absence of air it is very stable, but when mixed with combustible bodies it deflagrates on heating. Dried hydrated osmium dioxide has the composition OsO<sub>2</sub>.2H<sub>2</sub>O, and is gradually oxidised in air to the tetroxide (Ruff and Bornemann, *Zeitsch. anorg. Chem.* 1910, 65, 429).

Osmium tetroxide OsO<sub>4</sub>, sometimes erroneously termed *osmic acid*, is prepared by heating finely-divided osmium in air or steam, or by dissolving it or the lower oxides in *aqua regia*. It may also be formed by fusing the metal with potassium hydroxide and nitrate: the mass is dissolved in water, precipitated with alcohol, and oxidised with chromic acid in a current of oxygen. The pure tetroxide so formed, when treated with potassium hydroxide, forms *potassium osmate* K<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O (Ruff and Bornemann, *l.c.*). The oxide forms glistening needles, which sublime readily, and give a colourless solution in water, possessing a caustic taste, and turned yellow by sulphur dioxide, then brown, green, and finally indigo-blue. When fused it boils at 100°, emitting a vapour of a powerful penetrating smell which attacks the lungs and eyes, and produces inflammation of the mucous membrane. The tetroxide also acts violently on the skin, causing painful wounds (Deville and Debray, *Ann. Chim. Phys.* 1859, [iii.] 56, 400; *Compt. rend.* 1874, 78, 1509). It is readily reduced to the lower oxides.

Osmium trioxide OsO<sub>3</sub> is unknown, but the corresponding *osmic acid* H<sub>2</sub>OsO<sub>4</sub> is formed, according to Moraht and Wischin (*Zeitsch. anorg. Chem.* 1893, 3, 153), by treating the potassium salt with nitric acid. Ruff and Bornemann (*l.c.*) state, however, that they could not obtain it. A number of its salts, the *osmates*, are known.

**Halides.** Osmium dichloride OsCl<sub>2</sub>, a dark brown insoluble powder, may be formed by heating the trichloride at 500° under pressure, and cooling the vapour at -50°; or in small quantity by heating the metal in chlorine.

Osmium trichloride OsCl<sub>3</sub> is formed when ammonium osmichloride is heated at 550° in chlorine (Ruff and Bornemann; see also Moraht and Wischin, *l.c.*). It is readily soluble in water and gives rise to the double salts known as the *osmochlorides* or *chlorosmates* M<sub>2</sub>OsCl<sub>6</sub>.

Osmium tetrachloride OsCl<sub>4</sub> is prepared by heating osmium in a slow current of chlorine at 650°-700°, the issuing vapours being cooled in a tube wrapped in asbestos. It forms black metallic crusts, volatilises in a vacuum to a yellow vapour, and is slowly decomposed by water with formation of the dioxide and hydrochloric acid. It gives the series of salts known as the *osmichlorides* or *chlorosmates* M<sub>2</sub>OsCl<sub>6</sub> (Gutbier and Maisch, *Ber.* 1909, 42, 4239). For certain derivatives of these and other similar compounds, see Rosenheim and Sasserath, *Zeitsch. anorg. Chem.* 1899, 21, 122; Wintrebert, *Ann. Chim. Phys.* 1903, [vii.] 28, 15.

Osmium bromides and iodides are also known.



**Iodo-osmious acid**  $\text{I}_2\text{Os} \cdot 2\text{HI}$  is formed when nascent hydrogen iodide reacts with an osmium compound. Its solution possesses a fine emerald-green colour, which rapidly turns red on exposure to air, but its salts are more stable and form permanent green solutions. This reaction may be employed as a test for osmium compounds and also for iodides in the presence of chlorides and bromides (Alvarez, *Compt. rend.* 1905, 140, 1254; Orloff, *Chem. Zeit.* 1907, 31, 1063).

**Osmium tetrasulphide**  $\text{OsS}_4$  is an insoluble brown substance formed by passing sulphuretted hydrogen into a solution of the oxide.

**Osmium sulphite**  $\text{OsSO}_3$  and numerous complex sulphites have been prepared (Rosenheim and Sasserath, *l.c.*; Rosenheim, *ibid.* 1900, 24, 420). Osmium forms complex derivatives with ammonia and also an acid  $\text{OsNO}_3\text{H}$ , termed *osmiamic acid*, a number of the salts of which have been prepared (Wintrebert, *ibid.* Ber. 1901, 34, 2698; *ibid.* the action of acids on the osmiamates, *nitrilo* compounds of osmium are formed (Brizard, *Ann. Chim. Phys.* 1900, [vii.] 21, 311; Werner and Dinklage, *l.c.*).

**Osmium nitrite**  $\text{Os}(\text{NO}_2)_2$  and complex nitrites and *nitroso* derivatives are also known (Wintrebert, *l.c.*; and *Compt. rend.* 1905, 140, 585). Osmium also forms a series of *osmocyano*ides very similar to the ferrocyanides. *Osmium oxalates* have been prepared by Wintrebert (*ibid.* 1900, 131, 264). Z. K.

#### OSMOSIS v. SOLUTION.

#### OSONES v. CARBOHYDRATES.

#### OSTEOLITE, Calcium orthophosphate,

$\text{Ca}_3(\text{PO}_4)_2$  v. CALCIUM.

#### OTTO OF ROSES v. OILS, ESSENTIAL.

**OUABAÏO.** The poison of the Somalis. Along the whole of the west coast of Africa, especially in the country of the Somalis, occurs a tree used by the natives for the preparation of their arrow-poison, and called by them Ouabaïo. Its wood is yellowish-white, very hard and dense, odourless, but possessing a strong bitter taste. Arnaud has isolated from it (*J. Soc. Chem. Ind.* 1889, 211; 1888, 586) *ouabain*,  $\text{C}_{30}\text{H}_{46}\text{O}_{12}$ , which has a physiological action similar to that of strophanthin, but which is twice as toxic, the poisonous dose being about 0.2 mgrm. per kilo. of body-weight (*ibid.* 1888, 765)—Cathelineau, *J. Pharm. Chem.* 1889, 436; *J. Soc. Chem. Ind.* 1890, 101. Ouabain is also obtained from *Strophanthus glaber*, by extracting the seeds, from which the oil has been removed by pressure between filter paper, by shaking with alcohol for several days at a temperature not exceeding 60°. The extract is distilled and the syrupy residue is taken up with water at 50°, filtered, evaporated in a dry vacuum and recrystallised from water (Arnaud, *Compt. rend.* 1888, 107, 1162).

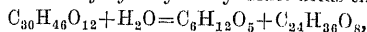
The crystals obtained by extracting *Strophanthus gratus* (Baill.), with 96 p.c. alcohol also seem identical with ouabain (Thoms, *Chem. Zentr.* 1904, i. 1277).

Ouabain forms pearly glistening plates, m.p. 185°–188°, and yields a crystalline hydrate with 9 molecules of water at ordinary temperature, with 4 molecules at 30° and with 3 molecules at 60°.

The rotatory power of a 1 p.c. aqueous solution of ouabain is  $[\alpha]_D -30.6^\circ$ . Ouabain is very

sparingly soluble in ether, absolute alcohol, and in chloroform; 100 c.c. of water dissolves 1.57 grams ouabain at 30°; 0.93 grams at 14.5° and 0.66 grams at 8°.

It is readily hydrolysed by dilute acids thus:



forming rhamnose and a red resin which is probably formed by the polymerisation of the second product of hydrolysis (Arnaud, *Compt. rend.* 1898, 126, 346, 1208). When dried, the resin loses  $4\text{H}_2\text{O}$  and forms  $\text{C}_{24}\text{H}_{32}\text{O}_4$ . Alkalis do not attack ouabain in the cold, but by forming soluble salts they increase its solubility in water and it

fused with potash or soda, at 220°–240° forming oxalic acid, a resin and carbon dioxide (Arnaud, *l.c.* 1280).

With bromine, ouabain gives an amorphous derivative containing 60 p.c. of halogen.

Heated with an excess of acetic anhydride at 30°–70°, ouabain forms the *heptacetin*,  $\text{C}_{30}\text{H}_{40}(\text{C}_2\text{H}_3\text{O})_7$ , m.p. 270°–275° (Arnaud, *l.c.* 310). When ouabain is heated with acetic anhydride and zinc chloride at 70° and the cooled product poured into 5–6 times its bulk of water, it forms an *acetin*,  $\text{C}_{30}\text{H}_{40}(\text{C}_2\text{H}_3\text{O})_6$ , m.p. 311° (in alcoholic solution).

On saponification, this acetin yields an acid which is similar to, but not identical with, ouabaic acid (Arnaud, *l.c.* 1654).

Concentrated nitric acid completely oxidises ouabain even in the cold, forming oxalic acid, carbon dioxide and insoluble amorphous nitro derivatives. With more dilute acid (sp. gr. 1.2), no oxalic acid is formed and insoluble crystalline nitro derivatives are produced.

The *di-nitro derivative*,  $\text{C}_{30}\text{H}_{44}(\text{NO}_2)_2\text{O}_8$ , is formed at 40°–75° and crystallises from acetone in yellowish silky needles, m.p. 300° (decomp.). It acts as a dibasic acid and yields crystalline salts. The potassium and sodium salts form orange-red aqueous solutions, the ammonium salt crystallises in golden yellow needles. The *mononitro derivative*  $\text{C}_{30}\text{H}_{45}(\text{NO}_2)\text{O}_8$  is obtained at 15° or below. It forms yellow anhydrous crystals, m.p. 280° (decomp.) and also yields alkali and ammonium salts. These nitro-derivatives are regarded as derived from the compound  $\text{C}_{24}\text{H}_{34}\text{O}_8$  which is the product of the hydrolysis of the ouabain.

**Ouabaic acid**  $\text{C}_{30}\text{H}_{44}\text{O}_{12}$  is obtained by heating a dilute aqueous solution of ouabain in a sealed tube at 180°, or better, by heating 1 part of crystalline ouabain with 3 parts of strontium hydroxide in 10 parts of water for 12 hours at 100°. The hot solution is saturated with carbon dioxide, filtered, concentrated *in vacuo* and poured, little by little, into a large volume of absolute alcohol. The precipitated strontium salt is dissolved in water with sulphuric acid; it is then filtered, and the liquid evaporated *in vacuo*. It is an amorphous, yellow-white substance, m.p. 235° (decomp.), resembling gum in appearance, very soluble in water and in alcohol, but insoluble in ether. It is a dibasic acid which decomposes the alkali and alkaline earth carbonates, forming the corresponding metallic salts. The barium salt,  $\text{Ba}(\text{C}_{30}\text{H}_{44}\text{O}_{12})_2$  has  $[\alpha]_D^{20} -46.40^\circ$  in aqueous solution (Arnaud, *l.c.* 1280).

According to Faust (Chem. Zentr. 1902, ii. 1217), *acocantherin*, isolated from *Acocanthera abyssinica* (K. Schum.), is homologous with ouabain, being, possibly, the dimethyl derivative. For the physiological and therapeutic action of ouabain v. Hatcher and Brody, Amer. J. Pharm. 82, 360; Müller, Zeitsch. Allgem. Österr. Apoth. Ver. 1908, 46, 319, 331.

**OUTREMER.** *Ultramarine* (q.v.); also Pigments.

**OVARIA SICC., OVARINUM, OVARADEN, OVADIN** v. SYNTHETIC DRUGS.

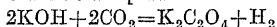
**OXALIC ACID**  $C_2H_2O_4$ , or  $COOH$



This acid occurs as the acid potassium salt in wood-sorrel, garden rhubarb, and many other plants. As calcium oxalate, it occurs in many lichens and in certain urinary calculi, and in the free state is found in *Fomes (Polyporus) igniarius*, in beet leaves, and in the juice of the chick pea. It is one of the constituents of the 'organic non-sugar' in the saccharine products from beet-roots, and to about 2 p.c. in 'saturation mud' of sugar refineries. It is also produced in the oxidation of a large number of a large number of bacilli (Zopf, Ind. 1900, 386; Banning, *ibid.* 1901, 1151); and also by the action of many fungi and yeasts (Lindner, *ibid.* 1907, 628).

It is obtained as an alkaline salt when an alkaline formate is gently heated, and as the ammonium salt when an aqueous solution of cyanogen is kept for some time. The sodium salt is produced by passing carbon dioxide over sodium heated to 360°. The free acid is one of the principal products of the action of nitric acid and other oxidising agents on organic matter.

**Preparation.**—Moissan has synthesised potassium oxalate by the direct union of carbon dioxide and potassium hydroxide at 80°–200° in accordance with the equation—



(Compt. rend. 140, 1209). Ir oxalic acid may be obtained by 8 parts of nitric acid of sp.gr. white sugar or starch, heating the mixture to boiling, and evaporating to about one-sixth the original bulk. The crystals obtained on cooling are recrystallised. If stronger acid be used the action is liable to become unmanageable.

This process was formerly employed on the manufacturing scale but has since been superseded by other processes; although possibly the discovery of Naumann, Moeser, and Lindenbaum (D. R. PP. 183022, 208999) that vanadium pentoxide to the extent of 0.001 to 0.002 gram per gram of sugar greatly facilitates the reaction, may give it a new lease of life. By this means, the reaction proceeds at the ordinary temperature, higher yields of oxalic acid are obtained, and no intermediate products result.

The first process to replace it was the well-known one in which sawdust is heated with caustic alkalis. Starch, straw, bran, and other vegetable matters may be similarly treated, but the best results are obtained with sawdust; fir, pine, poplar, and other soft woods, giving better results than hard woods, such as oak and beech. In order to obtain a finer product, the sawdust

is sometimes treated with an alkaline lye to remove resinous and like bodies before fusion.

This process has received many modifications, the chief one being the addition of some oxidising agent. An improvement is patented by Plater-Syberg (Eng. Pat. 23682, 1893). The material is, especially wood and moss, is caustic alkalis and then heated in presence of an oxidising agent. Hot air, or a mixture of steam and hot air, may conveniently be used as the oxidising agent. Acetates and oxalates are formed, the relative proportion of each depending on the temperature employed. By working at about 120°, acetic acid and a very small quantity of oxalic acid are formed. On raising the temperature to about 300° and increasing the quantity of hot air, the formation of acetic acid almost entirely ceases, whilst oxalic acid is formed in large quantity. Pulp suitable for paper making is obtained as a

of Plater-Syberg's process is that of Zacher (Eng. Pat. 2308, 1897), in which the oxidising material is sodium peroxide or hydrogen peroxide and the heating is carried out in a vacuum. Sawdust or other cellulose material is placed in a steam-jacketed vessel which is exhausted. The contents are then slowly raised to about 70° to deprive the sawdust of moisture and air. Hot alkali lye is then admitted with continued stirring and the vacuum kept constant until a temperature not exceeding 180° is reached. Towards the end of the process, an oxidising agent such as sodium peroxide, hydrogen peroxide, or air enriched with oxygen is admitted. The finished product is dissolved in water in the same vessel, and the solution forced into an open stirring cylinder, in which it is thinned and treated with lime. The calcium oxalate obtained, practically free from carbonate, is decomposed by sulphuric acid. It is stated that a good white oxalic acid is produced by this process with one recrystallisation (v. also D. R. P. 103856).

Another method is to oxidise the cellulose-containing materials, in solution of caustic soda or potash of sp.gr. 1.04 to 1.1, with permanganates or manganates. The yields are better than those obtained by heating with caustic potash alone and a much lower temperature is required (Droste, D. R. P. 199583).

Oxalates are also produced together with other products by the process of Cross and Young (Eng. Pat. 28077, 1902). A nitrate or mixture of nitrates is mixed with a carbohydrate of the sugar type, an alkali or alkaline earth, and a little water, and the mass is gradually heated—ultimately to 150°–170°. The main products in this case are cyanide and oxalate. The addition of iron to the mixture produces an excess of cyanide, and the addition of sulphur, or a sulphur compound, a thiocyanate. Ammonia is evolved during the process.

A process for the preparation of oxalic acid and cellulose (Lifschütz, Eng. Pat. 1824, 1891) consists in treating wood, jute, straw, and similar materials with a mixture of dilute nitric and sulphuric acids. The brown vapours evolved, consisting of NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub>, are reconverted into nitric acid. The acid liquid is used for other operations, the temperature being gradually increased as the

nitric acid becomes exhausted. When this occurs the oxalic acid is crystallised out by cooling. The ligneous material after the action of the nitric acid is converted into cellulose by treatment with a weak alkaline solution.

A completely different method is that of Goldschmidt (Eng. Pat. 26172, 1897). Sodium formate is prepared by the patentee's method of heating sodium carbonate under pressure in a current of carbon monoxide (Eng. Pat. 17066, 1895). 4 parts of crystallised sodium formate are then intimately mixed with 5 parts of anhydrous sodium carbonate and rapidly heated in a molten lead bath at 400°-410°. Air is preferably excluded and the hydrogen evolved is collected. The equation is  $\text{Na}_2\text{CO}_3 + \text{HCOONa} \rightarrow \text{Na}_2\text{O} + \text{CO} + \text{Na}_2\text{O} + \text{HCOONa}$ . The sodium carbonate is then washed out with water at 200°.

An improvement on Goldschmidt's method is patented by Wiens who heats formates with previously produced oxalates, in place of sodium carbonate, at 360°-410° (U. S. Pat. 714347, 1902). Koepp and Co. heat the formates with small quantities (less than 5 p.c.) of alkali hydroxide. The mixture rapidly melts, hydrogen is evolved at about 290° and the reaction is complete at 360°, occupying about half an hour in all (Fr. Pat. 331498, 1903; U. S. Pat. 748791, 1904; Eng. Pat. 9327, 1903).

Feldkamp (U. S. Pat. 802980, 1905) simplifies the sodium formate method of manufacturing oxalates by heating caustic soda in a current of carbon monoxide and dioxide (water gas or producer gas). The resulting mixture of sodium formate and carbonate is afterwards heated to a higher temperature until the evolution of hydrogen ceases, and a mixture of oxalate and carbonate is produced. The caustic alkali is then regenerated by the addition of slaked lime and precipitated calcium carbonate and oxalate decomposed (U. S. Pat. 802980, 1905; also Fr. Pat. 358735, 1905).

The process of Bitterfeld finds that oxalates are speedily and evenly produced from formates by heating in a partial vacuum to a temperature of about 280°. Processes with sodium carbonate or oxalate are improved by working in a vacuum, but the best results are obtained by heating the formate alone (Eng. Pat. 19943, 1907; Fr. Pat. 381245, 1907; D. R. P. 204895).

Materials containing cellulose, such as peat, vinasses, sawdust, can be made to yield oxalic acid by treatment with caustic soda or potash in the presence of lime, nitrates, metallic oxides, and air between 170°-190° (Eiffont, Fr. Pat. 373157, 1906).

Hempel's process consists in heating caustic soda and carbonate of soda or analogous substances with carbon monoxide under pressure. At 200°-380°, formates are produced, and at higher temperatures up to 420°, oxalates. Oxalates are also produced by heating formates with or without the addition of indifferent substances at 200°-420° under pressure (Fr. Pat. 389039, 1908; Eng. Pat. 3429, 1908; 4897, 1908; 3904, 1908).

Oxalic acid is usually obtained from the oxalates resulting from these processes by dissolving them in water and precipitating as

calcium oxalate, which is filtered off, washed, and decomposed with sulphuric acid. The solution is then filtered, evaporated, and allowed to crystallise. Other methods are used to some extent. McDougall and McDougall obtain oxalic acid by first preparing the potassium salt, adding a suitable sulphate (e.g. aluminium sulphate), and sulphuric acid, and separating the resulting alum by crystallisation, adding alcohol if necessary (Eng. Pat. 17971, 1907).

Another method is to add hydrofluoric acid, which precipitates the alum as artificial cryolite,  $\text{Na}_3\text{AlF}_6$  (G. Mith, D. R. P. 214040). The crude acid is usually somewhat dirty from adherent mother-liquor. It is separated therefrom by a centrifugal cleanser, washed with a minimum quantity of cold water, and recrystallised.

The acid cannot be purified from oxalates by ordinary recrystallisation, but requires to be crystallised from hydrochloric acid of 10 to 15 p.c., which retains the bases as chlorides. A second crystallisation removes the acid. The pure acid may also be prepared by sublimation as described below, or by decomposing the methyl or ethyl ester with water.

For the preparation of pure oxalic acid, Schmatolla recommends crystallisation from absolute alcohol containing a drop or two of sulphuric acid, followed by crystallisation from water, the solution being allowed to stand for several hours in both cases. The crystals are then dried at 30°-40°, and finally over calcium chloride (J. Soc. Chem. Ind. 1901, 496). Riechelmann prefers to crystallise once from ether and once from water (Chem. Soc. Abstr. 1898, i. 239).

**Properties.**—Oxalic acid crystallises in large transparent monoclinic prisms of sp.gr. 1.641 at 4° (Joule and Playfair), containing two molecules of water.

In an atmosphere dried by sulphuric acid, it gradually loses its water. The water is also gradually evolved and the crystals become opaque when heated at 60° or 70°. As the crystals melt in their water of crystallisation at 98°, and are then somewhat difficult to desiccate, it is advisable to dry the crystals at the lower temperatures. Saturated solutions of oxalic acid lose acid even on the water-bath. The anhydrous acid (dried as above) may be volatilised at 157°, and be thus obtained in pure white needles. The temperature should not be allowed to exceed 157°, as considerable decomposition ensues and an inferior product is obtained at 160°.

When oxalic acid is dissolved in 12 parts of warm concentrated sulphuric acid, the solution gradually deposits glistening rhombic pyramids of the anhydrous acid, which rapidly absorb two molecules of water and fall to powder.

Oxalic acid dissolves readily in water and in 2½ parts of cold alcohol. It is also slightly soluble in ether, but is insoluble in chloroform, benzene, and petroleum spirit.

The following table gives the solubility of oxalic acid in water as averaged by Seidell from the results of Alluard; Miczynski (Monatsh. 1886, 7, 258); Henry (Compt. rend. 99, 1157); Lamouroux (*ibid.* 128, 998); and, at 25°, of Foote and Andrew (Amer. Chem. J. 1905, 154):—

°	Grms. (COOH) <sub>2</sub> per 100 grms.		°	Grms. (COOH) <sub>2</sub> per 100 grms.	
	H <sub>2</sub> O	Solution		H <sub>2</sub> O	Solution
0	3.45	3.33	40	21.15	17.46
10	5.55	5.26	50	31.53	23.97
20	8.78	8.07	60	45.55	31.37
25	11.36	10.21	70	63.82	38.95
30	13.77	11.91			

Oxalic acid is a powerful reducing agent. The aqueous solution is oxidised at the ordinary temperature in presence of peroxides of lead and manganese. It precipitates gold from solution of the chloride, and, in sunlight, similarly reduces platinum chloride. In presence of sulphuric acid it is oxidised by potassium permanganate with production of carbon dioxide and manganese and potassium sulphates. Oxalic acid is not acted on by sulphuric acid at the ordinary temperature, but when heated with the strong acid it is converted into carbon monoxide and carbon dioxide, darkening the acid. Phosphoric acid and phosphorus penta- and tri-chloride also cause the evolution of these gases. Chlorine is without action on the anhydrous acid, but in presence of water it is reduced to hydrochloric acid, and evolution of carbon dioxide and chlorides of easily reducible metals, such as gold and platinum, have a similar action; bromine water slowly oxidises oxalic acid to carbon dioxide and hydrobromic acid.

When exposed to bright light, oxalic acid solutions are decomposed, yielding carbon dioxide and water (Douns and Blunt. Proc. Roy. Soc. 28, 209); by oxidation with nitric acid of sp.gr. 1.4 and upwards, oxalic acid is completely decomposed into these products. According to Richardson (Chem. Soc. Trans. 1894, 452), hydrogen peroxide acts similarly (cf. however, Jorissen and Reichler, Chem. Zentr. 1904, i. 81); the reaction is greatly accelerated by metals (O. Sulc. *ibid.* 1899, i. 1150). Certain substances have the property of accelerating the decomposition of oxalic acid.

Ind. 1891, 25), and an examination of a number of substances has been made by Jorissen and Reichler (Chem. Zentr. 1904, i. 359). Oxalic acid is reduced by nascent hydrogen to glycollic acid.

Solutions of oxalic acid are precipitated by phosphates, chlorides, and carbonates. When heated with sodium or calcium chloride, the powdered acid liberates hydrochloric acid. Potassium and sodium, when heated with the dry acid, cause an evolution of hydrogen with production of a carbonate, the temperature rising to incandescence.

When heated with glycerol between 70° and 90°, oxalic acid is converted into formic acid with evolution of carbon dioxide.

The commercial acid and alkaline oxalates frequently contain organic matters which cause charring when heated alone or with sulphuric acid. Sulphates of calcium, barium, and lead and other heavy metals also occur. Allen has found as much as 1% of lead oxide in a sample of the acid.

Oxalic acid is largely used as a 'discharge' in calico-printing and dyeing, and for bleaching flax and straw. In dyeing it is used as a substitute for cream of tartar, on account of its

cheapness. In the process of 'chroming' wool, its utility lies in its power of forming double salts and in its reducing properties (Körner, J. Soc. Chem. Ind. 1895, 1044). Its property of accelerating the action of chromic acid on indigo is probably due to the formation of a chromium compound of oxalic acid with strong oxidising properties (Prud'homme, *ibid.* 1903, 359, 491; v. also Georgevics, *ibid.* 947). The function of oxalic acid in the process of 'chroming' wool has also been studied (ibid. 1893, 758); and Jorissen and Reichler (*ibid.* 1902, 1276); and Jorissen and Reichler (*ibid.* 1903, 623). Werner (Chem. Soc. Trans. 1904, 1388) finds that by the action of chromic acid on oxalic acid, an acid chromic oxalate, H<sub>6</sub>Cr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>, is produced, and his results are confirmed by Jorissen and Reichler (Chem. Zentr. 1904, i. 81). It is also employed for whitening leather, for making formic acid and its esters, and for removing ink or iron stains from fabrics, marble, &c. A solution of Prussian blue in oxalic acid is employed as a blue ink. Oxalic acid forms a constituent of several dyes. Georgevics has prepared a dye-stuff which is yellow in colour, by heating resorcinol with oxalic acid at 160° (J. Soc. Chem. Ind. 1898, 837). It has great cleansing power for brass and other metal, and even for wood-work, and forms a constituent of at least one soap composition for cleaning metals, &c.

**Detection and Estimation.**—Solutions of calcium salts, even of calcium oxalate, precipitates of calcium oxalate, but solutions of oxalates, soluble in mineral acids but not in acetic acid. Free oxalic acid is precipitated by lime water and calcium acetate, but it is better to render the solution alkaline by ammonia and acidify with acetic acid before testing. Pure oxalic acid and oxalates do not char when heated alone or with concentrated sulphuric acid. It decolorises permanganate on warming. Silver nitrate produces with neutral solutions a white crystalline precipitate of silver oxalate which is very explosive when dry.

For the estimation of oxalic acid, the hot dilute solution, after being neutralised with ammonia and then acidified with acetic acid, is precipitated with calcium chloride or acetate, or, when sulphates are present, with calcium sulphate. For the estimation in presence of interfering substances, reference must be made to standard works on analysis. After standing for 12 hours, the precipitate is filtered off and dried, and is ignited at a dull, scarcely visible red heat to convert it into carbonate. A little saturated solution of ammonium carbonate is then added to reconvert into carbonate any of the substance which may have become causticised, and the mass is dried and heated sufficiently to remove the whole of the ammonium salt. When the precipitate does not exceed a gram, it is ignited at a bright-red heat over the blow-pipe and weighed as oxide. The ignited precipitate may also be titrated with standard acid.

Another excellent method consists in dissolving the moist precipitate in dilute sulphuric acid and titrating with standard potassium permanganate.

This method is not applicable to oxalates of oxidisable substances are absent.

Another alternative is to add dilute sulphuric acid to the precipitate in the crucible in sufficient quantity to convert it into calcium sulphate, and subsequently to ignite and weigh as calcium sulphate.

Hydrochloric acid is generally held to interfere with the volumetric estimation of oxalic acid, but according to Baxter and Zanetti (Amer. Chem. J. 1905, 500) oxalic acid may be estimated in the presence of hydrochloric acid with accuracy by titration with permanganate at the initial temperature of

70° and the permanganate is run in slowly. The concentration of the hydrochloric acid should not exceed 20 c.c. dilute acid (sp.gr. 1.04) to 150 c.c. oxalic solution, containing not more than 0.3 gram crystallised oxalic acid. Gooch and Peters recommend the addition of a manganese salt (Zeitsch. anorg. Chem. 21, 185). Oxalic acid is occasionally an impurity in hydrogen peroxide in which it may be detected and estimated by nearly neutralising, adding ammonium acetate and subsequently calcium acetate, and treating the calcium oxalate by any of the well-known methods (Roche, J. Soc. Chem. Ind. 1902, 190). Oxalic acid may be estimated in acid beet leaves by the method of Schlössing (Bilow, *ibid.* 1900, 383). The methods of determination in diffusion sugar juice are reviewed by Andrelik and Stanik (*ibid.* 1900, 178).

#### OXALATES.

This extensive series of salts includes both normal, acid, and double oxalates, and a class of acid salts known as quadroxalates, and apparently produced by the combination of one molecule of oxalic acid with one molecule of an acid oxalate. All oxalates decompose on heating, the alkaline salts forming carbonates. Only a limited number of oxalates are of technical importance.

**Potassium oxalate**  $C_2O_4K \cdot 2H_2O$  occurs in monoclinic prisms or pyramids, readily soluble in water. The acid salt  $C_2O_4HK$  is found in rhubarb, sorrel, and other plants. It occurs either in anhydrous, monoclinic prisms, or in triclinic crystals containing one molecule of water. The acid salt, which is much less soluble than the normal salt, forms with oxalic acid *potassium quadroxalate*  $C_2O_4KH \cdot C_2O_4H_2 \cdot 2H_2O$ , which forms triclinic crystals soluble in 20 parts of water at 20°.

Both these acid salts are sold as 'salts of sorrel' or 'salts of lemon,' and are used for removing ink stains, &c., and also for scouring metals, cleansing wood, &c., for which they are at least as suitable as the free acid.

The normal salt may be prepared by neutralising the acid with potash or potassium carbonate. The acid salt may be made by halving a solution of the acid, neutralising one part, and adding the other to a solution of the normal salt, or by adding 75 parts of potassium chloride to 252 parts of oxalic acid, both in saturated solution. Potassium oxalate is employed in the hot bath used in the platinotype process, and is also used in other photographic operations (v. PHOTOGRAPHY).

**Sodium oxalate**  $C_2O_4Na_2$  occurs in various plants growing in salt marshes. It and the acid

salt are prepared similarly to the potassium compounds.

**Ammonium oxalate**  $C_2O_4(NH_4)_2 \cdot 2H_2O$  has yet been prepared. The normal salt requires about 36 parts of cold water for solution. It separates from hot solutions in fine glistening needles or as a crystalline powder. The acid salt is still less soluble.

**Ammonium oxalate**  $C_2O_4(NH_4)_2 \cdot 2H_2O$  occurs in Peruvian guano. It crystallises in long rhombic prisms readily soluble in water. The acid salt is less soluble, crystallises in rhombic prisms and gives a quadroxalate isomorphous with that of potassium. These salts are prepared similarly to the potassium salts.

**Calcium oxalate**  $C_2O_4Ca$  is widely distributed in the vegetable kingdom and is the least soluble of the oxalates. It occurs in rhubarb and other plants, frequently in aggregations of needle-like crystals. In larger proportions it occurs in many lichens which grow on limestone, and in certain urinary calculi. It is precipitated as a powder containing one molecule of water, by addition of a calcium salt to an oxalate. When heated to 180° it becomes anhydrous, but it reabsorbs water when exposed to the air. The acid salt has not been prepared.

**Barium and strontium oxalates** resemble the calcium salts, but are somewhat soluble in water. The neutral *magnesium oxalate*, and double oxalates of magnesium with potassium and ammonium but not with sodium, are known. The acid magnesium oxalate has not been prepared.

**Ferrous oxalate** occurs in lignite combined with  $1\frac{1}{2}H_2O$  as *oxalite* or *humboldtine*. It may be prepared as a heavy yellow, nearly tasteless powder, almost insoluble in cold, and sparingly soluble in hot water, by mixture of ferrous sulphate with oxalic acid or an oxalate; or in fine lemon-coloured crystals by exposure of a solution of hydrous ferric oxide in oxalic acid. It is also slowly deposited from a solution of iron in oxalic acid. The artificial variety contains  $2H_2O$ . An acid oxalate appears to exist.

Ferrous oxalate is employed as a developer in photography. The solution used is obtained by adding ferrous sulphate solution to excess of potassium oxalate. The ferrous oxalate exists in the resulting brown solution as a double ferrous potassium oxalate  $K_2Fe(C_2O_4)_2 \cdot 2H_2O$ . When heated it is converted into a very finely divided oxide, admirable as a rouge for optical purposes.

**Ferric oxalate.** The normal salt is slowly deposited as a yellow precipitate on mixing a normal oxalate with ferric chloride, or on treating freshly precipitated ferric hydroxide with a quantity of oxalic acid insufficient to dissolve the whole. The solution in oxalic acid gradually deposits ferrous oxalate on exposure to the light. Double salts with the alkalis are obtained by solution of ferric hydroxide in acid alkaline oxalates. These are considerably used in photography in the preparation of platinum printing papers. *Sodio-ferric oxalate*

$Na_3Fe(C_2O_4)_3 \cdot 4\frac{1}{2}H_2O$  forms large green crystals. The ferric ammonium oxalate is sometimes used instead of the double citrate for producing blue prints in photography.

**Antimony oxalates.** The application of antimony oxalate and the double oxalates with

the alkaline metals in calico-printing has been noted under article **ANTIMONY**, vol. i. The normal salt  $\text{Sb}_2\text{O}_3 \cdot \text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  is obtainable by boiling antimonious chloride or oxychloride in oxalic acid, or by mixing a saturated solution of oxalic acid with a hydrochloric acid solution of the trichloride. It crystallises out as a granular precipitate. The antimony potassium oxalate  $\text{SbK}_3(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  is obtained in monoclinic crystals from a solution of antimonious acid in acid potassium oxalate. It is used as a mordant in dyeing. The sodium salt  $\text{SbNa}_4(\text{C}_2\text{O}_4)_4 \cdot 10\text{H}_2\text{O}$  is similarly prepared.

**Cerium oxalate**  $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  is a white, slightly granular, insoluble powder, permanent in the air, odourless and tasteless. It may be prepared by the action of oxalic acid solution on cerous oxide, or by addition of oxalic acid to a soluble cerium salt. Cerium oxalate has medicinal properties resembling those of bismuth subnitrate, and is used to prevent the vomiting of pregnancy and in certain diseases (Jolin, Bull. Soc. chim. [ii.] 21, 540).

**Methyl oxalate**  $\text{C}_2\text{O}_4(\text{CH}_3)_2$  is obtained in rhombic tables melting at  $54^\circ$  and boiling at  $163^\circ$  by dissolving anhydrous oxalic acid in methyl alcohol and washing the crystals with cold water. Methyl oxalate is converted into oxalic acid and methyl alcohol by boiling with water. Pure oxalic acid may thus be prepared (v. **METHYL**).

**Ethyl oxalate**  $\text{C}_2\text{O}_4(\text{C}_2\text{H}_5)_2$  is a liquid which may be obtained by slowly heating a mixture of 3 parts of the anhydrous acid and 2 parts of absolute alcohol to  $100^\circ$ , afterwards heating to  $125^\circ$  or  $130^\circ$  while the vapour of 2 parts of absolute alcohol is passed in. The ethyl oxalate is separated by fractional distillation. This compound is an aromatic oily liquid boiling at  $186^\circ$  and decomposed by water in the same manner as methyl oxalate.

A great number of aromatic esters of oxalic acid have been prepared and characterised by Bischoff and Hedenström (Ber. 1902, 3437); and also by Anselmino (Ber. Deutsch. Pharm. Ges. 1903, 494).

The decomposition of oxalates on heating, though taking place approximately according to the equation  $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$  in the case of calcium oxalate is in reality more complex. Some carbon is always produced during the ignition of calcium oxalate. Sodium and barium oxalates follow the courses  $7\text{Na}_2\text{C}_2\text{O}_4 = 7\text{Na}_2\text{CO}_3 + 3\text{CO} + 2\text{CO}_2 + 2\text{C}$  and  $8\text{BaC}_2\text{O}_4 = 8\text{BaCO}_3 + 6\text{CO} + \text{CO}_2 + \text{C}$ . Magnesium oxalate gives equal volumes of CO and  $\text{CO}_2$  and no carbon,  $\text{MgC}_2\text{O}_4 = \text{MgO} + \text{CO} + \text{CO}_2$ ; but most other oxalates give notable quantities of carbon dioxide and carbon (Scott, Chem. Soc. Proc. 1904, 156).

The electrolytic reduction of oxalic acid and oxalates in sulphuric acid solution to derivatives of glyoxylic acid was first patented by Porthelm (U.S. Pat. 798920, 1905).

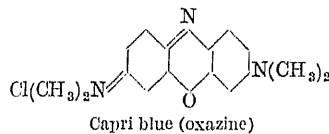
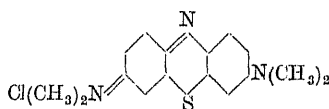
Kinzlberger and Co. (D. R. P. 163842) reduce oxalic acid, its esters, and amide electrolytically in a cell with a lead cathode and a diaphragm in presence of sulphuric acid of strengths varying from 2 to 90 p.c. monohydrate. The current density is 2 to 10 amps. per sq. cm. and the temperature must be kept low. Oxanilic acid or its derivatives in the same conditions yield phenylglycine or a derivative (v. also U.S. Pat.

837083; D. R. PP. 204787, 194038). Kinzlberger & Co. have since secured an additional patent for the use of electrodes of metals not attacked by sulphuric acid, particularly mercury (D. R. P. 210693). Bayer & Co. make use of sodium amalgam in the reduction of oxalic acid derivatives (D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176).

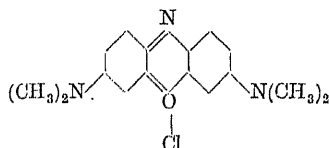
#### OXALIC ACID FERMENTATION v. FERMENTATION.

#### OXAMINE BLUE, -MAROON, -RED, -VIOLET v. AZO-COLOURING MATTERS.

**OXAZINE COLOURING MATTERS.**—The colouring matters of this series are closely related in structure to those of the thiazine group, the only difference in their general formulæ being caused by the replacement of the coupling sulphur atom by oxygen. Two typical examples in Capri blue and methylene blue will illustrate this statement



**Constitution.**—The formula for Capri blue given above represents this substance as a derivative of *p*-quinone-diimide in which salt formation is produced on the imido nitrogen as in, for example, magenta. Within recent years, attempts have been made to assign to the oxazines an ortho-quinone formula of the same character as that which has been accepted as best expressing the constitution of the colouring matters of the azine series. On this basis the formula of Capri blue becomes



in which salt formation is represented as having taken place through the passage of diad into tetrad oxygen. The work of Kehrman and others shows that many of the properties of these compounds can be better explained by the oxonium formula than by the para-quinone structure. In the present article the oxonium formulæ have been used mainly for the sake of uniformity, although it must be remembered that it is by no means certain that the para-quinone structure of the salt is incorrect.

**General description and methods of preparation.**—The colouring matters of the series may be conveniently classed under two heads: (a) the basic colours; (b) the mordant colours.

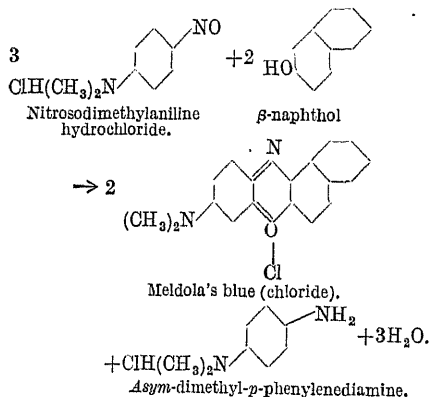
(a) **The basic colours.**—These compounds are the hydrochlorides, sulphates, and, in some cases, the zinc chloride double salts of the oxazines

bases. The most typical member is **Meldola's blue**, which was prepared by Meldola in 1879 and was the first colour of the series to be isolated. In the first instance the preparation was effected by allowing  $\beta$ -naphthol to react with nitrosodimethylaniline hydrochloride in glacial acetic acid solution. At the present time alcohol is used as a solvent and the colour is obtained by the

... containing 21 grams of  $\beta$ -naphthol and 53 grams of nitrosodimethylaniline hydrochloride is dissolved in alcohol and boiled for one day in a flask fitted with a reflux condenser. The colouring matter is formed in solution and is isolated as the zinc chloride double salt by adding a solution of zinc chloride until no further precipitate is obtained. The yield is 30 grams.

**Properties.**—The colour is a dark violet powder, soluble in water forming a bluish-violet solution. It dyes cotton mordanted with tannic acid and tartar emetic an indigo shade of blue.

**Mechanism of formation.**—There is no doubt that the formation of an oxazine colouring matter, in the manner described above, involves the reduction of one-third of the nitrosodimethylaniline used to *asym*-dimethyl-*p*-phenylenediamine and that the equation representing the formation of Meldola's blue can be written as follows:—



It is advisable, however, to use a larger quantity of nitrosodimethylaniline than is indicated in the above equation and to employ two molecules of the aniline derivative to one of the naphthol in all reactions of this type.

**Literature.**—Meldola (Ber. 1879, 12, 2065; Chem. Soc. Trans. 1881, 39, 37); Nietzki and Otto (Ber. 1888, 21, 1745); Witt (*ibid.* 1890, 23, 2247); Nietzki and Bossi (*ibid.* 1892, 25, 2994). Meldola's blue appears in commerce under other names of which the following are the more important: new blue, naphthylene blue, fast blue, cotton blue, fast navy blue and naphthol blue.

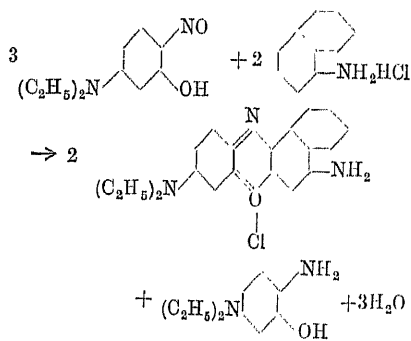
It is evident from the above equation that the formation of an oxazine colouring matter of the type of Meldola's blue might be expected to ensue when any derivative of  $\beta$ -naphthol is treated with a derivative of nitrosodimethylaniline provided that in the one case the adjacent position to the hydroxyl group is unoccupied

and in the other the ortho-position to the nitroso group is free. In practice, however, the formation of colours of this character is confined to the simpler reaction. Nevertheless, a new method for the preparation of these colours was introduced by Reissig in 1888, and by its means a number of important colours were added to the group. The new process can be best illustrated by referring to the production of **Nile blue A**, which is produced by the interaction of

**Preparation.**—A quarter litre flask, fitted with an air condenser, containing 10 grams of nitrosodimethylaniline hydrochloride dissolved in 100 c.c. of water, is heated on the water-bath. The contents are at the boiling-point when 19 grams of  $\beta$ -naphthol are added. The vigorous reaction which is caused by each addition is allowed to subside before a fresh portion is added. When all the phenol has been used the mixture is allowed to boil for half an hour when the colouring matter separates as glistening crystals on cooling.

**Properties.**—Crystalline powder, with marked bronze reflex, soluble in water, alcohol or pyridine forming a blue solution. Dissolves in concentrated sulphuric acid forming an orange-red solution which, on dilution, passes through green to blue. It is employed for the dyeing of tanned cotton on which it produces a bright shade of blue.

**Mechanism of formation.**—The production of Nile blue A may be expressed by an equation similar to that given in the case of Meldola's blue, as shown below:



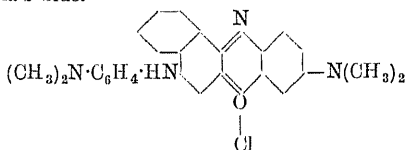
**Literature.**—Reissig (B. A. S. F.), E. P. 4476, 88; 11046, 91; Am. P. 431541, 90; D. R. P. 45268, 88; 74391, 91; F. P. 189359, 88; Bayer, D. R. P. 49844, 89; F. P. 198589; Möhlau and Ullmann (Annalen, 289, 111); Thorpe (Chem. Soc. Trans. 1907, 91, 324). The commercial product is usually the sulphate.

Other members of class (a) may be summarised as under; they are employed as tannin cotton colours.

**Capri blue** is formed from nitrosodimethylaniline and diethyl-*m*-aminocresol (Bender, 1890), and the **Cresyl blues** (Bender, 1892) are derived from nitrosodialkyl-*m*-amino-*p*-cresol and meta- or para-dianilines.

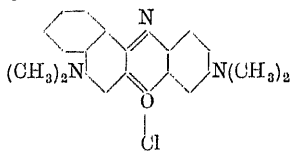
**New blue R** is formed by the condensation of

*asym*-dimethyl-*p*-phenylenediamine with Meldola's blue.



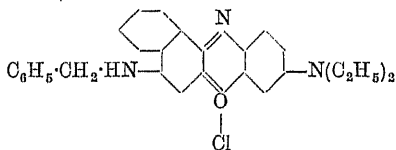
It has been already stated that this base is a by-product in the formation of Meldola's blue. It therefore follows that New blue is always present in small quantities in commercial Meldola's blue.

New methylene blue is formed by the action of dimethylamine on Meldola's blue.

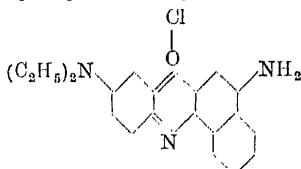


It dyes cotton mordanted with tannin a greenish-blue, fast to light and washing and is also employed for the dyeing of silk.

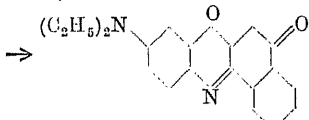
Nile blue 2B is formed by the condensation of *asym*-dimethyl-*p*-phenylenediamine with Meldola's blue hydrochloride and *asym*-dimethyl-*p*-phenylenediamine (Julius, 1891)



The basic colours of this series have been used for some considerable time as stains for the purpose of colouring microscope sections; like other basic colours, they stain the nitrogenous parts of the section leaving the neutral regions uncoloured. It has been shown by Lorrain Smith (J. Path. Bact. 1907, 12, 1) that certain colours of the oxazine series possess the curious property of staining sections containing nitrogenous matter and neutral fat differentially; that is to say, whilst the nitrogenous matter is coloured blue in the usual manner the neutral fat is stained red. The colouring matter which exhibits this property to the greatest degree is Nile blue A, and there is no doubt that the cause of this behaviour is due to the partial hydrolysis of the dye in solution, thus—



Nile blue A (chloride).—Blue.



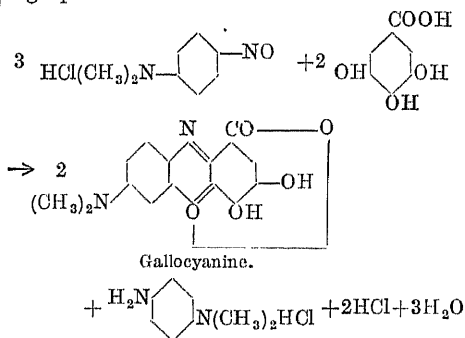
The phenonaphthoxazone.—Red.

It is found (Chem. Soc. Trans. 1907, 91, 324) that small quantities of the oxazine are formed so soon as the dye is dissolved in water and that it is readily extracted by neutral solvents. It is evident, therefore, that the staining of the neutral fat is due to the extraction of the oxazine by the fat.

(b) *The mordant colours*.—The colouring matters of this section are prepared by the condensation of *asym*-dimethyl-*p*-phenylenediamine with compounds of the *asym*-dimethyl-*p*-phenylenediamine type. The oxazine contains, therefore, two hydroxyl groups in the ortho- position to the coupling oxygen atom; consequently, like alizarin, they yield insoluble lakes with metallic salts and can be employed as mordant colours. A typical member of this group is **Gallocyanine**, which can be prepared by the condensation of nitroso-dimethylaniline with gallic acid.

*Preparation*.—A mixture of 10 grams of gallic acid and 17 grams of nitrosodimethylaniline hydrochloride is dissolved in 200 c.c. of alcohol (95 p.c.) contained in a 500 c.c. round-flask which is fitted with a reflux condenser. The reaction is completed by heating on the water-bath until a drop, removed by the aid of a glass rod, shows a deep violet spot, without a yellow rim, when placed on filter paper. The alcohol is then distilled off on the water-bath, and the dried residue, after being boiled with 200 c.c. of water and separated by filtration, is dried on porous porcelain. The colouring matter is a bronze powder insoluble in water. It dyes chrome-mordanted wool bluish-violet, and is also used for printing upon chrome-mordanted wool and cotton.

*Mechanism of formation*.—The course of the reaction, which is of the same character as that already shown, can be illustrated by the following equation—



*Literature*.—H. Köchlin, D. R. P. 19580, 1881; E. P. 4899, 1881; Am. P. 253721, 257408; Mon. Scien. 1883 (3) 13, 292; Nietzki and Otto (Ber. 1888, 21, 1736; 1892, 25, 2994).

The other dyestuffs of this group are, for the most part, derived either directly from gallocyanine by the action of various reagents, or by processes in which gallic acid or a derivative of this substance is employed. The following are the more important members.

**Delphine blue** (Hagenbuch, 1889) is prepared by sulphonating the product formed by the action of gallocyanine hydrochloride on aniline. The **Chromocyanines** (de la Harpe and Vaucher,

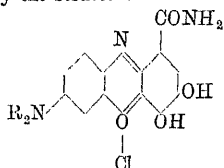


1898) are formed by the action of sulphites on galloxyanines.

**Indalizarin** (de la Harpe and Vaucher, 1900) is obtained from the galloxyaniline sulphonic acids by the action of sulphites.

**Gallamine blue** (Geigy, 1889) is formed by the action of nitrosodimethylaniline on gallamide.

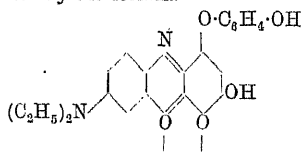
**Coreine 2R** (Bierer, 1893) is the corresponding diethyl derivative. It is probable that the formulæ of these compounds is best expressed by the structure—



**Coreine AR** is derived from Coreine 2R by the action of aniline.

The **Phenocyanines** (de la Harpe, 1893) are obtained by the action of resorcinol on the galloxyaniline which is formed by the condensation of nitrosodiethylaniline and gallic acid.

**Phenocyanine VS** is the initial product, and **Phenocyanine TC** is formed from this by the oxidising action of air; its structure is probably represented by the formula

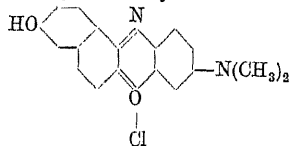


**Phenocyanine TV** is the sulphonic acid of Phenocyanine TC.

**Gallanilic violets** (Möhler, 1889) are formed by the action of nitrosodialkylanilines on the anilide of gallic acid. The further action of aniline produces **Gallanilic blue**.

The above colours are largely used for the dyeing of chrome-mordanted wool on which they produce various shades of blue and violet. The colouring matters given below also belong to the oxazine series—

**Muscarine** (Annaheim, 1885) is prepared by the action of nitrosodimethylaniline hydrochloride on 2-7-dihydroxynaphthalene. Its structure is represented by the formula

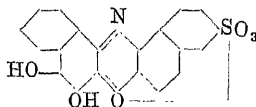


It is employed in the dyeing of tanned cotton on which it produces a fairly fast shade of blue.

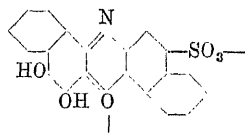
**Fast Green M** (Bierer, 1894) is derived from muscarine by the action of aniline. Printed on cotton in conjunction with tannin, this colour produces a fine fast shade of green.

The **Alizarin Greens** (Elsässer, 1895) are prepared from  $\beta$ -naphthoquinone sulphonic acid and certain amines. Thus **Alizarin Green G** is formed when  $\beta$ -naphthoquinone sulphonic acid is condensed

with 2-amino-1-naphthol-4-sulphonic acid and is represented by the structure

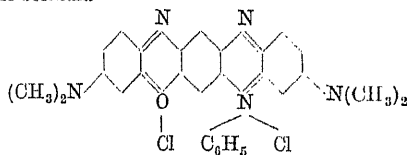


**Alizarin Green B** is formed from the corresponding 2-amino-1-naphthol-4-sulphonic acid and has the structure



Both colouring matters produce fast shades of green on chrome-mordanted fabrics.

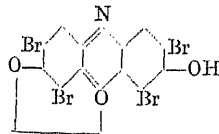
**Fast Black** (Bender, 1889) is formed by the condensation of nitrosodimethylaniline with *m*-hydroxydiphenylamine. The structure of this compound is, in all probability, represented by the formula



The dye-stuff produces an extremely fast shade of blue-black on tannin-mordanted cotton.

**Resorcin Blue** (Ullrich, 1898) is always produced directly on the cotton fibre by treating the material, with resorcin, and resorcin, with

**Fluorescein** (Benedict, 1888) is a compound which is produced by heating nitrosoresorcinol with resorcinol in the presence of concentrated sulphuric acid. It has the structure



and dyes silk and wool a fairly bright shade of blue, the dyed fabric retaining, to a certain extent, the brownish fluorescence of the dye solution. J. F. T.

**OX-GALL** v. BILE.

**OXIDISED OILS** v. OILS, FIXED, and FATS.

**OXINDOLE** v. AMINO ACIDS (AROMATIC).

**OXONITE** v. EXPLOSIVES.

**OXOZONE** v. OZONE.

**OXYACANTHINE**  $C_{18}H_{19}NO_3$ . An alkaloid associated with berberine and berbamine in berberis root (Hesse, Ber. 19, 3190).

**OXYANTHRARUFIN**. *Oxychrysazin* v. ALIZARIN AND ALLIED COLOURING MATTERS.

**OXYAZO-DYES** v. AZO-DYES.

**OXYCAMPHOR** v. SYNTHETIC DRUGS.

**OXYCANNOBIN** v. RESINS.

**OXYDASES**. The term 'oxydase' was first applied by Bertrand to the group of oxidising ferments which possess certain characteristics

common to enzymes. Although there is much in the behaviour of the oxydases which distinguishes them sharply from other enzymes, particularly the fact that they are generally associated with manganese, it is customary to regard them as enzymes and to define them as substances which, under physiological conditions, rapidly carry oxygen to materials on which otherwise oxygen would act very slowly.

Oxydases act as catalysts, their activity rises to an optimum with increase of temperature and then falls with a further rise: it is destroyed on boiling. They are insoluble in alcohol, absorbed by colloidal precipitates and unable to diffuse. Usually, they are selective in their action, oxydases acting only on certain groups of more or less closely related materials.

The power of effecting oxidation is accompanied by the liberation of oxygen from the material.

Oxydases are so universally distributed and take part in so many natural phenomena, particularly those which are manifested externally by colour changes, that it is surprising so little is understood as yet about the mechanism of their action. A number of reagents have been employed in their study: few of these are really satisfactory.

The most extensively used are guaiacum, which gives a blue colouration and precipitate; quinol, which is oxidised to quinone (Bertrand, *Compt. rend.* 1894, 18, 1215); pyrogallol, which gives insoluble purpurogallin (Bach and Chodat, *Ber.* 1904, 37, 1342); vanillin, which forms insoluble vanillinol (Herzog and Meier, *Zeitsch. physikal. Chem.* 1908, 57, 35; 1909, 59, 57). The behaviour of tyrosinase is studied on tyrosine which becomes first red, then black and finally gives a black precipitate. Salicylic aldehyde, benzidine, the leucobase of malachite green, phenolphthalein, &c., have also found employment. [For a complete list of oxydase reagents and references to the original papers, *v. Kastle*, U. S. Treasury Dept. Hygienic Laboratory, Bulletin No. 59.]

The better known oxydases are:—

1. *Laccase*, which oxidises guaiacum, quinol, tannin, &c., and is very widely distributed in plants.
2. *Tyrosinase*, which oxidises tyrosin and allied substances: it occurs in both plants and animals. Less studied have been—
3. *Aldehydease*, an animal oxydase, which oxidises salicylaldehyde and other aromatic aldehydes.
4. *Indophenol oxydase*, which is widely distributed in animal tissues: it forms indophenol from  $\alpha$ -naphthol and  $p$ -phenylenediamine (Röhmman and Spitzer, *Ber.* 1895, 28, 567). In addition, enzymes known as *peroxydases*, which oxidise reagents only in presence of a peroxide like hydrogen peroxide, are universally distributed in living cells and tissues.

The view is gaining ground that oxydases are not entities but in reality mixtures of a peroxydase and an unstable organic peroxide (Moore and Whitley, *Biochem. J.* 1909, 4, 136; Bach and Chodat, *Ber.* 1903, 36, 606). Many plants contain organic bodies capable of autoxidation, thereby becoming organic peroxides. This superoxidation may be caused by an enzyme—

the *oxygenase*. These *oxygenases*, peroxide and peroxydase, are distinguished by the substitution of an oxydase.

*Catalases* are ferments which decompose hydrogen peroxide but cannot effect the oxidation of oxydase reagents, a distinction first drawn by Loew (Bulletin No. 66, U. S. Dept. Agric. 1901). They are very widely distributed in vegetable and animal tissues. Catalase is soluble in water and destroyed by heat. Considerable interest attaches to the catalase (hemase) of blood (Senter, *Zeitsch. physikal. Chem.* 1903, 44, 257; 1905, 51, 673).

It has been suggested that the function of catalase is to protect the organism against excessive oxidation, but the inability to decompose substituted organic peroxides or oxygenases (Bach and Chodat, *Ber.* 1903, 36, 1756) and other facts make this view and the question is as yet not understood.

*Peroxydases* and catalases are so widely distributed in tissues that their presence might almost be used as a chemical test for vital activity. They are characterised by great stability: thus the peroxydase of horse-radish is not entirely destroyed when its solution is boiled for a short time. The activity of a weak oxydase is greatly increased by a peroxydase, moiety of which from the same source as the oxydase usually lose their activity during the process which they bring about.

Peroxydases appear invariably to contain manganese, and Bertrand (*Compt. rend.* 1897, 124, 1032, 1355) has shown that the oxidising power of laccase is due to the amount of manganese present: that the addition of manganese greatly increased the oxidising power of lucerne laccase. He therefore regards manganese as the co-ferment of laccase in the same way as hydrochloric acid is the co-ferment of pepsin. The manganese cannot be replaced by other metals in the case of laccase, but iron and other metals have similar functions with other enzymes. Colloidal suspensions and solutions of these metals have been shown to form artificial laccase. The subject is a complex one, see *Kastle, l.c.*

**Tyrosinase.** An oxidising ferment acting on tyrosine is widely distributed in both plants and animals. When the enzyme is added to a solution of tyrosine, the mixture becomes red, then black and deposits finally a black precipitate. The amount of action is conveniently measured by titrating with 0.002 normal potassium permanganate after the addition of sulphuric acid (Bach, *Ber.* 1908, 41, 216) until the colour of the titer disappears.

This change is responsible for the reddening and subsequent blackening observed in certain fungi and in the roots and tubers of plants. Tyrosinase is also of importance in the formation of animal pigments, inasmuch as they are termed (v. *von Fürth* and Schneider, *Beitr. chem. Physiol. Path.* 1901, 1, 229; also von Fürth and Jerusalem, *ibid.* 1907, 10, 131).

Tyrosinase is entirely different from laccase which usually accompanies it in plants. The peroxydase of laccase activates hydrogen peroxide towards guaiacum, quinol, pyrogallol, &c., but not towards tyrosine, whilst the peroxydase of tyrosinase acts only on tyrosine and certain

amino compounds and does not affect the laccase reagents.

Vegetable tyrosinase is best obtained from *Agaricus* or *Agaricus*—or from *Agaricus* and Mutermilch, Compt. rend. 1907, 144, 1385). The young fresh fungus is macerated with chloroform water or with glycerol, or the enzyme may be precipitated from the aqueous extract by alcohol (Bach, Ber. 1908, 41, 221). 300 c.c. of clear expressed fungus juice is poured into 1.5 litres of 96 p.c. alcohol: the precipitate is filtered, washed with alcohol and dried in a vacuum. The activity depends on the age of the fungus.

To obtain it from wheat bran, 1 part is allowed to stand with 4 parts water—the mixture is centrifuged and the solution mixed with 3 vols of 95 p.c. alcohol. The precipitate is separated, washed, and dissolved in distilled water. The enzyme is again precipitated by alcohol, collected and dried *in vacuo*: the substance obtained amounts to 0.8 p.c. and contains no laccase.

Sources of animal tyrosinase are the ink sac of the cuttle fish and the pupae of the butterfly of the species *Deiciphilia euphorbie* (von Fürth and Jerusalem, l.c.).

Tyrosinase is sensitive to the action of acids and alkalis and certain poisons, particularly hydrocyanic acid. It obeys the laws of mass action in the production of melanin from tyrosine (Bach, Ber. 1908, 41, 221).

Tyrosinase acts on dextro- and levo- colours with compounds analogous to tyrosine containing a phenolic hydroxyl (Bertrand, Bull. Soc. chim. 1908, [iv.] 3, 335). It gives colour changes with homogentisic acid and tryptophane and with polypeptides containing tyrosine; the latter are not coloured like tyrosine but become yellow, then orange and finally mahogany red. The nature of the amino acid modifies the colour (Abderhalden and Guggenheim, Zeitsch. physiol. Chem. 1907, 54, 331; also Chodat and Staub, Arch. Sci. Phys. Nat. 1907, 23, 265; 1907, 24, 172).

Laccase is of almost universal distribution in the vegetable kingdom but its occurrence in animals is rare. It is soluble in water and active aqueous extracts are readily obtained from most plant materials, the potato and cabbage being convenient sources. It is more stable towards heat and alcohol than tyrosinase, the latter being destroyed at 70°: laccase is killed on boiling. Most acids and substances, such as hydrogen cyanide and hydrogen sulphide, destroy its activity.

It may be salted out from solution by ammonium sulphate. It is not specific in its action but promotes the oxidation of a large number of easily oxidisable substances. It is responsible for the colour changes occurring in cut fruits like apples, pears, &c., the brown colour formed being considered to be due to the oxidation of tannin by laccase (Lindet, Compt. rend. 1895, 120, 370; Kastle and Loevenhart, Amer. Chem. J. 1904, 31, 606).

A very complete and critical summary and bibliography of the literature bearing on oxydases is given by J. H. Kastle, Bulletin No. 59, Hygienic Laboratory, U. S. Treasury Dept. 1910. E. F. A.

## OXYGEN. Sym. O. At.wt. 16.

*Historical note.*—The first recognition of the rôle of oxygen in nature would seem to date from the eighth century. The Chinese Philosopher Mao-Khóa then promulgated a theory based on his experiments, that all matter was composed of two fundamental elements, Yang (the strong or primary) and Yin (the weak or secondary). In air both these elements were present combined with elemental fire. The Yang (or more complete air) could be obtained purer by burning in air certain of the metals, sulphur or charcoal, which robbed the air of some of its Yin; whilst Yin, never occurring pure in the air, could be obtained by heating certain minerals (the identity of which is not clear) and especially Hhò-siaò (probably nitre). Mao-Khóa recognised that the Yin of the air was also present in water, though here it was so closely bound to Yang that its separation was difficult. The important part taken by Yin in combustion and respiration was recognised. Leonardo da Vinci was the first European to recognise, towards the end of the fifteenth century, the non-elemental character of the air and to state that only one part of it was concerned in combustion and respiration. Robert Hooke, in Micrographia, published in London in 1665, recognised the same fact, and that the same

at least a very similar one, was present in nitre. Mayow in 1674 recognised that the active constituent of air which supports combustion forms only part of the atmosphere, and that the same substance is present in nitre, and is given off when nitre is heated strongly. Mayow termed this gaseous constituent of air and nitre *spiritus vitalis*, *spiritus nitro-aëreus*, and *pabulum igneo-aëreum*. Borch (1678) carried the work of Mayow rather further, and Hales (1727) obtained oxygen by heating nitre, and collected the gas over water in nearly theoretical quantity, but failed to recognise its character. Priestley obtained the gas on August 1, 1774, by heating mercuric oxide in a glass vessel by the heat of the sun's rays concentrated on the oxide by means of a burning glass, and gave it the name *dephlogisticated air*. The gas was isolated independently, and almost simultaneously, by Scheele in 1774, though the publication of this result was only made several years later, by the Swedish chemist Scheele, who applied to it the term *empyreal* or *fire-air*. Condorcet soon after suggested the name *vital air*. Lavoisier regarded it as an essential constituent of all acids, and hence gave it its present name *oxygen* (from *gēs*, acid, and *γεννᾶω*, I form). The later discovery that hydrochloric and the other halogen acids contained no oxygen showed that this substance is not necessarily present in acids, but the name has been retained. The discovery of oxygen was the means of leading Lavoisier to the true theory of combustion (see *Entdeckung des Sauerstoffes*, &c.).

*Occurrence.*—Oxygen is the most abundant and the most widely distributed element in nature. In the free state it occurs, mechanically mixed with nitrogen, in the atmosphere, of which it forms about 21 p.c. by volume, and more than 23 p.c. by weight. In the combined state it forms eight-ninths by weight of all the water on the globe, and nearly half of the three

chief constituents of the earth's crust, viz. silicious rocks, chalk, and alumina. Most minerals—the chief exceptions being rock salt, fluorspar, blende, galena.

Oxygen in considerable essential constituent of all animal and vegetable tissues and fluids. It is absorbed in large quantities from the atmosphere by animals and vegetables during respiration, but this abstraction is practically counterbalanced by the oxygen evolved by green foliage under the influence of sunlight.

*Preparation.*—A. *On the laboratory scale.* Oxygen may be obtained by the action of heat on the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, the alkalis, barium, lead, and manganese; the chlorates, bromates, iodates, nitrates, and dichromates of potassium and other bases; it is evolved during some chemical reactions, and during the electrolysis of many substances, notably of water.

Of the modes of preparation most convenient for use in the laboratory, or of interest from historical or theoretical considerations, the following are the principal:—

1. By heating red oxide of mercury it splits up into vapour of mercury (which condenses) and oxygen:  $2\text{HgO} = 2\text{Hg} + \text{O}_2$ . This reaction is of interest as being that by which Priestley first obtained oxygen.

2. By heating manganese dioxide to a bright-red heat it gives up one-third of its oxygen:  $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ . The oxide is best heated in an iron bottle placed in a furnace, as glass vessels will not stand the high temperature required. 100 parts by weight of the pure peroxide yield 12.3 parts by weight of oxygen.

Manganese dioxide occurs in large quantities in nature as the mineral *pyrolusite*, and thus forms a cheap source for the preparation of quantities of a few hundred feet of oxygen, but the high temperature required makes the process somewhat inconvenient. Pyrolusite usually contains about 70 p.c. of the dioxide, and therefore gives a lower yield of oxygen than that indicated by the equation.

3. Potassium chlorate is a very convenient and economical source for small quantities of oxygen for lecture and laboratory purposes. When gradually heated in a hard glass retort or flask, this salt melts at about  $360^\circ$ – $370^\circ$ , and at about  $370^\circ$ – $380^\circ$  evolution of oxygen commences. After some time the fused mass thickens from the formation of the perchlorate, which, at a still higher temperature, is also decomposed. Ultimately, therefore, potassium chloride alone remains in the generating flask, the whole of the oxygen having been given off according to the equation:  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ . 100 parts by weight of chlorate yield 39.16 parts by weight of oxygen, or 1 oz. of chlorate 1.8 gallons of the gas. The oxygen obtained is very pure.

The temperature required in this decomposition is too high for convenient use, as the glass vessels employed in the preparation of the gas often soften under the great heat, and yield to the pressure of the contained gas. When metallic vessels are used the heating must be very carefully watched, since the decomposition being exothermic (*i.e.* heat being evolved during the reaction), when once decomposition has set

in, the evolution of gas is liable to become very violent. If the potassium chlorate be mixed with about one-eighth its weight of some non-fusible oxide, such as oxide of copper, oxide of iron, or manganese dioxide, the evolution of oxygen takes place at about  $240^\circ$ , or considerably below that at which the salt fuses, and is much more regular. The addition of a little spongy platinum answers the same purpose.

The gas prepared in this way almost invariably contains traces of chlorine, which are removed, when necessary, by passing the gas through a solution of caustic soda.

Commercial manganese dioxide (*pyrolusite*) is sometimes adulterated with coal-dust. If such dioxide is heated with potassium chlorate the coal-dust burns—often with explosive violence—at the expense of the oxygen of the chlorate, and this has been the cause of fatal accidents. It is, therefore, advisable to test the dioxide before use by heating a small quantity in a test tube with some chlorate.

The action of these oxides in facilitating the decomposition of the potassium chlorate is probably due to the transient formation of higher oxides of extreme instability. The oxides which show this action most markedly are those which form unstable higher oxides. The action of spongy platinum is less clear, but is probably connected with the tendency of that substance to condense oxygen on its surface.

4. By heating a concentrated solution of bleaching powder (or any hypochlorite) to which a small quantity of oxide of cobalt has been added, it is resolved into calcium chloride and oxygen:  $2\text{CaOCl}_2 + 4\text{CoO} = 2\text{CaCl}_2 + 2\text{Co}_2\text{O}_3$  and  $2\text{Co}_2\text{O}_3 = 4\text{CoO} + \text{O}_2$ . The decomposition is shown in two stages to exhibit the action of the oxide of cobalt. It is not necessary to use pre-formed oxide of cobalt, as any salt of cobalt will answer the same purpose. The oxides of copper, iron, and nickel are similar in their action. Instead of a solution a thick paste of " " and water may be used if a " " if paraffin oil is added. The oil, floating on the surface of the pasty liquid, prevents the frothing which would otherwise take place. The best temperature for the evolution of gas is about  $70^\circ$ – $80^\circ$ , at which a steady stream may be obtained.

Another modification of this method is to pass a stream of chlorine into boiling milk of lime to which a small quantity of a salt of copper, cobalt, or nickel has been added. Oxygen gas is given off according to the equation  $2\text{Cl}_2 + 2\text{Ca(OH)}_2 = 2\text{CaCl}_2 + 2\text{H}_2\text{O} + \text{O}_2$ .

5. From various peroxides—

(a) When an intimate mixture of 3 mols. barium peroxide (2 parts by weight) and 1 mol. potassium dichromate (1 part by weight) is treated with dilute sulphuric acid, oxygen is " " at ordinary temperatures " " J. [ii.] 5, 436).

b. If 500 c.c. of commercial hydrogen peroxide (10 p.c. solution) are introduced into a suitable generating flask, and a solution of 25 grms. of potassium permanganate in 500 c.c. of water, mixed with 25 c.c. concentrated sulphuric acid, is allowed to flow gradually into the mixture from a dropping funnel, oxygen will be rapidly evolved without the application

of heat, the amount of oxygen obtained from these quantities being about 10 litres.

(c) Baumann recommends (Zeitsch. anorg. Chem. 1890, 79) charging a Kipp apparatus with pieces of pyrolusite of 2-4 mm. diameter and using as the activating liquid commercial hydrogen peroxide to which, while well cooled, 150 c.c. of strong sulphuric acid has been added per litre. The evolution of the oxygen is steady and continuous. Neumann recommends the use of cubes made from 2 parts barium peroxide, 1 part pyrolusite, and 1 part gypsum with hydrochloric acid of sp.gr. 1.12 as activating liquid, but the oxygen evolved by this method contains traces of chlorine.

(d) If water is dropped on to broken pieces of fused potassium, sodium or potassium-sodium peroxide, a steady stream of oxygen is evolved. Walter recommends fusing 100 grms. sodium peroxide, 100 grms. potassium nitrate, and 25 grms. magnesia; hydrochloric acid is then dropped on to the cold.

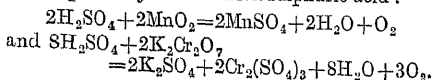
(e) If a mixture of equipercent parts of peroxide and a salt containing water of crystallisation, such as  $\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ , is gently heated, oxygen is evolved in a steady stream.

6. On passing a mixture of steam and chlorine through a red-hot porcelain tube, filled with fragments of porcelain to increase the heating surface, the chlorine combines with the hydrogen of the water and oxygen is liberated:  $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$ .

7. By the electrolysis of water slightly acidulated with sulphuric acid, the water is resolved into hydrogen and oxygen, the latter being collected in the inverted tube.

This forms a convenient method of obtaining small quantities of pure oxygen, such as are required in gas analysis.

8. Oxygen may be prepared from such highly oxidised compounds as peroxides of lead and manganese, potassium dichromate and permanganate, &c., by the action of sulphuric acid. These are, however, seldom used as sources of gaseous oxygen, but are very useful as oxidising agents. Thus hydrochloric acid, when treated with sulphuric acid and potassium permanganate, is oxidised to hypochlorous acid. Similarly, potassium dichromate treated with sulphuric acid and manganese dioxide yields aldehyde and water. The following equations represent the changes which take place when manganese dioxide and potassium dichromate are respectively treated with sulphuric acid:



The change is rendered visible in the latter case by the formation of a deep-green salt of chromium, the solution being previously of a red colour.

9. When fresh leaves, such as mint or parsley, are exposed to the influence of sunlight in an inverted cylinder filled with water saturated with carbon dioxide and standing in a basin of the same liquid, oxygen appears after a time in minute bubbles on the leaves, and collects in the upper part of the jar. This method of liberating oxygen is of interest as being that which occurs in nature, by means of which the loss of atmospheric oxygen continually taking

place from combustion and respiration is replaced.

Several other modes of preparation which, in addition to their theoretical interest, are of practical and technical value, will be treated of in the following section.

B. *On the industrial scale.* 1. The first method proposed for obtaining oxygen on the large scale was the ignition of nitre, and this method, in various modifications, has formed the basis of several patents. The first oxygen patent occurring in the records of our Patent Office, is No. 12536, S. White, 1849. But the oxygen so obtained was contaminated with oxides of nitrogen, and this method has not proved advantageous. It deserves mention, however, as being the means by which Priestley first obtained impure oxygen in 1771. He then believed the gas to be 'fixed air' (carbon dioxide), and only recognised his mistake 3 years afterwards, when he obtained oxygen from mercuric oxide.

2. By heating  $\text{HgO}$ . This was formerly one of the methods of preparing oxygen on the commercial scale.

3. By heating a mixture of potassium chlorate and about one-eighth of its weight of manganese dioxide. Though more costly than the last-named, this method is more easily carried out, and was, until within the last 30 years, almost exclusively employed in the preparation of the considerable quantities of oxygen used for lime-light purposes.

4. By heating  $\text{Fe}_2\text{O}_3$  of sulphuric acid by heat:  $\text{Fe}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{Fe}_2\text{O}_4 + \text{H}_2\text{O}$ . The sulphuric acid is decomposed on red-hot surfaces, and is thus decomposed. If the oxygen alone is wanted, the emergent gaseous mixture is passed over media suitable for the absorption of the water and sulphur dioxide. As a method for the preparation of oxygen only this process has not found much favour, but it has been very largely and successfully used in the preparation of sulphur trioxide, where, the water being removed by a desiccating agent, a mixture of sulphur dioxide and oxygen in the desired proportions is at once obtained. It is the process suggested by Squire in his patent for the manufacture of sulphur trioxide (Eng. Pat. 3278, 1875).

5. By the dialysis of air. Many attempts have been made to utilise the laws of diffusion of gases through porous septa, discovered by Graham, or the property of caoutchouc when in thin layers to allow oxygen to pass through it more readily than nitrogen. Several patents have been taken out for processes of this kind, but with no practical success, and the phenomena do not seem likely to lend themselves to the production of oxygen on the large scale.

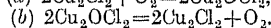
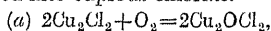
6. Better success has attended the endeavour to make use of the greater solubility of oxygen than of nitrogen in water or other solvents. Mallet, who took out a patent for this process (Eng. Pat. 2137, 1869), compressed the air over water. The coefficient of solubility of oxygen in water is about twice that of nitrogen. The oxygen was, therefore, dissolved in greater proportion than the nitrogen, and when the excess of pressure was removed and the dissolved gases extracted by the aid of a vacuum pump, the amount of oxygen in the gaseous mixture was greater

than in air. This mixture was then repeatedly subjected to the same treatment, when, after about eight absorptions, nearly pure oxygen was obtained. The following table, given by Mallet (Dingl. poly. J. 199, 112), shows the composition of the gaseous mixture at each successive stage of the operation :—

Atmo- spheric air	Composition after successive absorptions							
	1	2	3	4	5	6	7	8
N=79	66.7	52.5	37.5	25.0	15.0	9.0	5.0	2.7
O=21	33.3	47.5	62.5	75.0	85.0	91.0	95.0	97.3

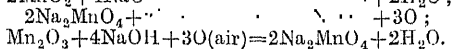
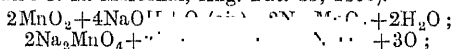
This process was used by Phillips in 1871-72 to obtain oxygen for his experimental lighting of part of Cologne by special oxygen-fed oil lamps, but beyond this does not appear to have been practically applied.

7. By the alternate oxidation and de-oxidation of cuprous chloride. Cuprous chloride, if exposed to air, and especially to moist air, is oxidised to cupric oxychloride, and this, when heated to dull redness, gives off oxygen, and is reconverted into cuprous chloride.



Mallet obtained patents (Eng. Pat. 2934, 1865, and 3171, 1866) for the practical utilisation of this method as a continuous process for obtaining oxygen from the air, but it has not been found economically available on the large scale.

8. By the alternate formation and decomposition of alkaline manganates. When an oxide of manganese is heated in proportions with a caustic alkali (potash or soda), and is subjected to the action of air at a moderately high temperature, an alkaline manganate is formed. If this manganate is then heated to a bright-red heat, and a current of steam passed over it, it is resolved into its original constituents with evolution of oxygen (C. M. Tessié du Motay and C. R. Marechal, Eng. Pat. 85, 1866).

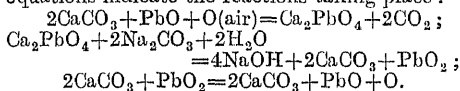


The mixture was introduced into horizontal retorts, which were heated to a dull-red heat while a current of air was passed through. After oxidation was complete the supply of air was cut off, the retorts were heated to a bright-red heat and a current of steam admitted when oxygen was evolved. The retorts were then allowed to cool again to a dull red, the passage of air again commenced, and so on. The mixture was said to undergo no deterioration, and a continuous and very economical method of obtaining oxygen seemed attained. Works were erected, and the process carried out on the large scale at Paris, Lille, Brussels, Vienna, and New York, and large quantities of oxygen were made. A large part of Paris was laid with a double system of piping with the intention of lighting that city with the oxy-hydrogen light, and the New York Company carried out by the same light the lighting of the works during the building of the Brooklyn bridge. But it was found in practice that the mixture did deteriorate, the yield of oxygen rapidly diminishing, and finally almost ceasing. This was probably due to the

retaining the intimate mixture of the hygroscopic and very soluble soda with the manganic oxide, the former settling to the bottom through the combined effect of the heat and steam used.

Many attempts have been made to overcome the difficulties of the manganate process. Bowman (Eng. Pat. 7851, 1890) claimed to have overcome this difficulty by making the alkaline manganate in a form and dusting over the still in a plastic condition, with oxide of copper. Parkinson (Eng. Pat. 14925, 1891) claimed improved modes of preparation of the material together with the use of a vacuum in place of steam to cause the evolution of the oxygen. The manganate material, in upright iron retorts, was heated to about 1200°, and air pumped in under pressure to effect oxidation, the pumps were then automatically reversed and the oxygen drawn off under greatly reduced pressure. Fanta's claim (Eng. Pat. 3034, 1891) mainly consisted in increased stability of the material by the use of excess of caustic soda, and Webb's resembled Bowman's, except that the pieces of manganate material were dusted over with manganese peroxide instead of with oxide of copper. In Chapman's process (Eng. Pat. 11504, 1892) 'oxide of manganese (or the like)' in a powdered form is kept suspended in fused soda (or the like) so that the charge is practically in the condition of a liquid, and the alternate supplies of air and steam were driven into the liquid at the bottom, thereby keeping the oxide in a state of suspension. But though these modifications have been tried on the practical scale, none of them has proved commercially economical.

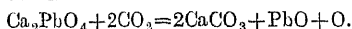
9. Kassner (Eng. Pat. 11899, 1889) found that when an intimate mixture of lead oxide and chalk is heated to 600° in contact with the air, a calcium plumbate  $\text{Ca}_2\text{PbO}_4$  is formed. If this plumbate is then introduced into a solution of potassium or sodium carbonate it is decomposed, an insoluble precipitate of calcium carbonate and lead peroxide is formed, and caustic potash or soda remains in solution. This is removed by decantation, and the precipitate washed. The precipitate, in which the lead peroxide is, of course, the active part, may then either be used directly as an oxidant, or it may be introduced into a decomposing vessel, dried with superheated steam, and heated to about 500°, when oxygen is evolved, the mixture of lead oxide and calcium carbonate left being then ready for regeneration. The decomposition of the plumbate may also be effected by suspending it in water and treating with carbonic acid. The following equations indicate the reactions taking place :



The inventor lays stress on the cheapness of the process owing to the caustic soda obtained being a valuable by-product. The complexity of the process and the large amount of labour entailed by it, leave very little chance of its being practically possible in chemical works, with the manufacture of here its economy is very doubtful.

The decomposition of the plumbate into lime and lead peroxide may also be effected *in situ* by means of a current of moist furnace gases at  $80^{\circ}$ – $100^{\circ}$ , and the oxygen then liberated by raising the temperature. The great changes of temperature, however, thus involved, render the method impracticable, and in addition the sulphur impurities in the furnace gases rapidly deteriorate the mixture.

Salamon (Eng. Pat. 6553, 1890) proposes to decompose the calcium plumbate without removing it from the producer in which it is formed by allowing the temperature to fall 'to a certain point,' and then introducing a current of pure carbon dioxide. The following reaction then occurs:



This necessitates the use of at least four times the volume of carbon dioxide as of oxygen obtained, a condition which at once puts the process out of the question as a technical and economical one. It has been suggested that the quantity of pure carbon dioxide required may be largely reduced by carrying out the earlier part of the reaction by means of the carbon dioxide in furnace gases, and using it pure only at the last. But the drawbacks so introduced fully neutralise any advantage.

10. By the alternate formation and decomposition of barium peroxide. In 1851 Boussingault found that when barium oxide (baryta) is heated to a dull-red heat in a current of air it is converted into barium peroxide, and that at a higher temperature this peroxide is again resolved into barium oxide and oxygen. But his attempts to utilise this reaction as a practical and economical source of oxygen failed owing to the fact that after a few oxidations and deoxidations the baryta lost its power of re-absorbing oxygen. Many other attempts were made to overcome this difficulty, but for long without success. In 1879, however, the MM. Brin frères were more successful, and took out a patent for the process (Eng. Pat. 1416 of 1880). Further improvements were made under the auspices of the company, and to develop and work the patents, and the process was made practical and economical, and was worked on a large scale at various places.

The decomposition of the baryta is mainly a physical condition, the use of reduced pressure during deoxidation, and consequent avoidance of high temperatures, and the air used. It is with change of

phases of oxidation the oxidation nor the deoxidation is as complete as when two temperatures are used, and the yield per operation is much less. But the duration of the operation was reduced from about 4 hours to 8–15 mins., and the total daily yield therefore largely increased. At the same time the operation was much simplified, the wear and tear of furnace, retorts, &c., very greatly reduced, and the fuel required lessened. Labour was also economised, the multiplied reversals of cocks, &c., necessitated by the old method of working being avoided by reversing gear designed by K. S. Murray. The labour

required was therefore little more than that needed for stoking the furnace, and oiling and supervising the pumps, &c. The oxygen obtained had a purity of about 93–96 p.c.

For a producer capable of delivering 10,000 cubic feet of oxygen per 24 hours the consumption of coke in the furnace is about 12–15 cwt. per day, and for plant of that or smaller size the pump power required is about 1 I.H.P. per 1000 feet of oxygen produced per day, the ratio decreasing for larger plants.

It is necessary that the barium oxide should be as hard and as porous as possible, and this is best obtained by igniting the nitrate. The decomposition soon commences with evolution of a mixture of oxygen and oxides of nitrogen. This action continues for about 2–3 hours, during which time the contents of the crucible remain in ebullition. A porous mass is then left, which is heated for another hour to complete, as far as possible, the decomposition. In this way a very hard but also very porous baryta is obtained.

This process was thoroughly practical and economical, and large numbers of plants were erected all over the world and worked successfully for many years. It was described in detail with illustrations of plant in the first edition of this dictionary (see also K. S. Murray, Proc. I. Mech. E. 1890, 131; Thorne, J. Soc. Chem. Ind. 1890, 246). Some plants are still working, but in the last few years the process has been largely superseded by the still cheaper liquid air process, which also produces oxygen of greater purity (*v. infra*).

*Cost of production.* It is very difficult to obtain data of the cost of production of oxygen under the earlier methods described, but the following figures probably approximate to the cost per 1000 cubic feet:—from chlorate 8*l.*–10*l.*, from pyrolusite 4*l.*–6*l.*; from sulphuric acid 2*l.* 10*s.*–3*l.* (probably only the oxygen and not the acid is utilised); by the Tessié du Motay process 3*l.*–4*l.*; by the Brin process 7*s.*–12*s.* No authentic data of the cost of producing oxygen by dialysis or by solution in water are obtainable, but it would be at least as high as that by the liquid air process. In the Kassner process the cost depends largely on the amount realised by the sale of the caustic alkali, but would certainly be prohibitive for technical purposes. For cost by the liquid air and electrolysis processes, *v. infra*.

*Properties.*—The International Committee on Atomic Weights has now adopted O=16 as the standard of comparison for all atomic weights, and under this scale H=1.008 (1.0076 Morley). Oxygen is a colourless, tasteless, and inodorous gas, of sp. gr. 1.1056 (air=1): at  $0^{\circ}$  and 760 mm. pressure a litre of the gas weighs 1.429 grms. (1.42893 at  $0^{\circ}$  and 760 mm., and 0.29071 grms. at  $1067.4^{\circ}$  and 760 mm., Jacquerod and Perrot, Compt. rend. 1905, 140, 1542), and at 30 ins. pressure and  $15.5^{\circ}$  100 cubic ins. weigh 34.206 grs. 1 grm. of oxygen measures 0.6997 litres and 1 lb. 11.84 ft. Oxygen also occurs in an active allotropic form called ozone, which is treated of in a separate article (*v. OZONE*).

Oxygen normally acts as a divalent element, but in many compounds, especially in many

organic compounds having somewhat basic characteristics, acts as a tetrad. When examined through very thick and highly compressed layers, gaseous oxygen has a slight blue tinge of colour. It is sparingly soluble in water. As with all gases, the quantity of oxygen dissolved by water depends on the tension of the oxygen in the atmosphere in contact with the water. Thus pure water shaken up in contact with pure oxygen will absorb nearly five times as much oxygen as it would when shaken up, at the same temperature and under the same pressure, with air—which only contains 20.9 p.c. by volume of oxygen. The following table gives the coefficients of solubility (*i.e.* the volume of oxygen absorbed by one volume of water when shaken up with pure oxygen under 760 mm. pressure) at different temperatures as determined by different observers:—

Temperature	Coefficient of solubility					
	Bunsen (1855)	Dittmar	Rosecoe and Lund	Winkler (1861)	Bohr & Boek (1891)	Fox (1905)
0°C.	0.0411	—	—	0.0489	0.0496	0.0492
10°	0.0325	0.0383	0.0377	0.0380	0.0390	0.0384
20°	0.0284	0.0312	0.0308	0.0310	0.0317	0.0314
30°	—	—	—	0.0262	0.0268	0.0267
40°	—	—	—	—	0.0233	0.0233
50°	—	—	—	—	0.0207	0.0209

These numbers multiplied by 1000 give at once the number of c.c. oxygen absorbed by a litre of water from pure oxygen.

The older numbers of Bunsen appear, from the results of more recent observers with more delicate apparatus, to be rather too low. Winkler gives the following formula for calculating the coefficient of solubility ( $\beta$ ) of oxygen in water at any temperature ( $t$ ).

$$\beta = 0.04890 - 0.0013413t + 0.0000283t^2 - 0.00000029534t^3.$$

Fox (Trans. Far. Soc. 1909, [v.] 68–81) gives the formula:—

$$\beta = 0.04924 - 0.0013440t + 0.000028752t^2 - 0.0000003024t^3.$$

The coefficient of solubility of oxygen in alcohol at 0° is 0.2337; at 20° it is 0.2201 (Timofejeff), so that oxygen is much more soluble in alcohol than in water.

Nearly all natural waters contain oxygen in solution and can only be freed therefrom by prolonged boiling *in vacuo*. This dissolved oxygen, though small in amount, is the source from which fish obtain the oxygen necessary to sustain life.

The solubility of oxygen in sea water at 16° is about 78 p.c. of its solubility in pure water (Clowes and Biggs).

Oxygen, though long regarded as a permanent gas, was liquefied in 1877 by Pictet at a pressure of 320 atmospheres, and a temperature of  $-140^\circ$ . Cailletet had a few days previously observed the formation of a mist due to liquefaction when oxygen at  $-29^\circ$  under a pressure of 300 atmospheres was allowed to expand suddenly. Olszewski in 1883 showed that the critical temperature of oxygen (*i.e.* the temperature above which no amount of pressure will liquefy it) is  $-113^\circ$ , the pressure needed to liquefy it

at that temperature being 50 atmospheres, and this was confirmed by Wroblewski and by Dewar in 1885.

Liquid oxygen is a pale steel-blue transparent and very mobile liquid showing a clear meniscus (Dewar; Olszewski) boiling at  $-182.5^\circ$  at 760 mm. pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen. Solidification takes place under 9 mm. pressure at  $-211.5^\circ$  (W.), under 172 mm. at  $-219^\circ$  (Dewar, Roy. Soc. Proc. 1911, 85, 589). This latter temperature is therefore the lowest obtainable by the evaporation of liquid oxygen. Travers, Sinter and Jacquerod (Proc. Roy. Soc. 1902, 70, 484) found the b.p. of oxygen to be  $-182.8^\circ$  at 760 mm.,  $-185^\circ$  at 600 mm.,  $-188.5^\circ$  at 400, and  $-193.8^\circ$  at 200 mm. Dewar obtained solid oxygen as a hard, pale-blue mass by cooling liquid oxygen in a spray of liquid hydrogen. Its m.p. is  $-219^\circ$  under a pressure of 1.12 mm. The density of liquid oxygen is 1.1181 at  $-182.5^\circ$ , 1.1700 at  $-195.5^\circ$ , 1.2386 at  $-210.5^\circ$ , and that of solid oxygen 1.4256 at  $-252.5^\circ$  (Dewar) corresponding to the general formula (for liquid and solid)  $d = 1.5154 - 0.00442T^2$  (where  $T^\circ$  = absolute temperature). 781.8 volumes of oxygen at 0° and 760 mm. are contained in 1 volume of liquid oxygen at  $-182.5^\circ$ . The latent heat of vaporisation of liquid oxygen varies with the temperature (Alt), at 760 mm. pressure (*i.e.*  $-182.5^\circ$ ) it is 50.97 cal., at  $-205^\circ$  it is 55.5 cal. The specific heat between  $-200^\circ$  and  $-183^\circ$  is  $0.347 \pm 0.014$ . The vapour density at  $-182^\circ$  is normal. The refractive index of liquid oxygen is 1.2236. Liquid oxygen absorbs nitrogen readily, absorbing at  $-190.5^\circ$  380 times its volume, or 42 p.c. of its weight of gaseous nitrogen, the b.p. being thereby reduced to  $-188.8^\circ$ . This was probably the cause of the discrepancies in the boiling-points given by the earlier observers. Liquid oxygen is a very perfect insulator, and is also comparatively inert in its chemical properties. Phosphorus, potassium, sodium, &c., may be immersed in it without any action taking place (Dewar).

When liquid oxygen is subjected to the action of strong light, and particularly of the ultra-violet rays, some of it is converted into ozone (Dewar). It is diathermanous, a non-conductor of electricity, but is strongly magnetic, its magnetic moment being 1 when iron is taken as 1000. The magnetic susceptibility of liquid oxygen at the freezing-point is 1.3 times as great as that of the solid. Its susceptibility is diminished as temperature is lowered, and is the least refractive of any liquid. It has a characteristic though not very strong absorption spectrum, but to obtain this it is necessary to view the source of light through great thicknesses of liquid or through the highly compressed gas. The spectrum first appears in the form of a number of fine lines, but as the pressure is increased or a layer of liquid oxygen is employed, it shows a number of broader and shaded dark bands, with absorption in the violet and blue. The absorption bands have been observed, two in the red corresponding to the A and B Fraunhofer lines. The absorption spectrum of liquid oxygen is practically identical



with that of gaseous oxygen. Oxygen shows a luminous spectrum in a Geissler tube containing a bright band in the red, two in the green, and one in the blue, but the spectrum varies under varying conditions.

The chemical activity of air depends upon the oxygen it contains, air being simply, in its chemical relations, oxygen diluted with nitrogen. Free oxygen, whether diluted with nitrogen or not, manifests considerable chemical activity, even at ordinary temperatures, this activity increasing with rise of temperature. There are only few elements—viz. fluorine, chlorine, bromine, iodine, silver, gold, platinum, neon, argon, and helium—which do not unite *directly* with oxygen. Most of the non-metallic elements unite with oxygen to form anhydrous acids. Of the exceptions, hydrogen forms a neutral oxide (water), whilst no oxides of fluorine, argon, neon, or helium have yet been obtained.

Phosphorus combines with oxygen at ordinary temperatures, as do also moist iron, moist lead, moist saw-dust, and many metallic compounds such as cuprous chloride, manganous

&c. This oxidation is called *autoxidation*, and substances undergoing autoxidation often induce the oxidation of other substances present which otherwise

The alkali metals are especially active in this way. In many cases ozone is produced. Light, and particularly

assists oxidation by gaseous oxygen. Potassium and sodium are at once attacked by dry oxygen at ordinary temperatures, becoming coated with their respective oxides. The majority of metals remain bright under similar conditions, but many become oxidised when moisture is present. In some of the metals oxidised by exposure to air the first coating of oxide formed acts as a protective covering and prevents further oxidation, as is the case with lead. In others, however, the oxide first formed gradually becomes converted into a higher oxide and may then give up part of its oxygen to the metal in contact with it, and the oxidation is thus propagated through the mass of the metal. The rusting of iron is not a simple case of oxidation (*v. Rust*). Some metals which in their ordinary condition are comparatively inert towards oxygen combine with it readily at ordinary temperatures when they are in a finely divided state, offering a very large surface for chemical action. Thus lead or antimony when obtained by the ignition of their tartrates, and iron, nickel, cobalt, and copper, when reduced from their precipitated oxides in a current of hydrogen at a low temperature, all ignite on contact with air or oxygen, and are therefore often termed *pyrophoric*. Silver, gold, and platinum are not acted on directly by oxygen at any temperature. Some metals in a molten state absorb considerable quantities of oxygen which is given out again wholly or in part when the metal solidifies. 10 grms. of molten silver at 1020° absorb about 20 c.c. oxygen (*v. Donnan and Shaw, J. Soc. Chem. Ind. 1910, 987*).

and palladium also absorb 450° silver gradually absorbs times its volume of oxygen,

gold 35–45, platinum 65–75, and palladium about 500 (7 p.c. by weight). Platinum black absorbs about 100 times its volume of oxygen and palladium sponge 1000, of which the whole is not given up again below a red heat. Wood charcoal absorbs oxygen at ordinary temperatures—about 18 times its volume (Goldstein)—but this absorptive power increases enormously at very low temperatures. At -185° 1 c.c. absorbs 230 c.c. of oxygen with the evolution of 34 cals., and this action may be employed to produce an oxygen vacuum, the pressure being reduced to that of a Geissler tube (Dewar).

The activity of substances (except under the conditions already mentioned) an initial heating is necessary to start free oxidation, the heat evolved during oxidation being then sufficient to maintain it. Thus iron heated to bright redness in an atmosphere or stream of oxygen takes fire and burns brightly. A mixture of oxygen and hydrogen may be kept at ordinary temperatures for any length of time without change, but if the temperature of any part of the mixture be raised to bright redness—either by the electric spark, by the presentation of a flame or by other means—ignition at once takes place with explosive force throughout the whole mass. Under certain circumstances, however, this combination may be effected at ordinary temperatures. Thus, if a piece of clean platinum foil be hung in the mixture, combination takes place gradually at ordinary temperatures. This appears to be due to the power possessed by platinum, and some other gases and especially the activity of the gases so condensed being thereby greatly increased. If platinum or palladium black or sponge is used instead of foil, the action is so much increased that the heat evolved in the combination soon raises the temperature of the metal to the ignition-point of the gaseous mixture, and ordinary combustion ensues. This effect has been taken advantage of in the *Döbereiner* lamp (named after the investigator who first noticed this property of platinum) wherein a piece of spongy platinum is suspended over a jet connected with an automatic vessel. When the tap is hydrogen becoming mixed with air and at the same time impinging on the spongy platinum, oxidation takes place rapidly, the platinum soon becomes red hot and ignites the jet of hydrogen. Similar effects are produced with oxygen (or air) and gaseous hydrocarbons.

Various substances which expose large surfaces to air (or oxygen) become gradually heated through slow oxidation or combustion, and, if the heat cannot get away, ignition eventually occurs. Thus oily or greasy woollen and cotton rags and refuse are capable of absorbing oxygen fairly rapidly, and if present in any quantity the heat produced may accumulate and cause spontaneous combustion, and this action is a not infrequent cause of fires in factories. A similar generation of heat and eventual 'spontaneous combustion' often arises from the storing of moist hay in haystacks, and from the storage of damp coal in ships or heaps. The allegation

that the ignition of coal is due to the oxidation of pyrites has been disproved by the work of Richters and Lewes, who have shown that the heat is generated by the absorption of oxygen and its action on the bituminous constituents of the coal.

Dixon, Baker, Traube, and others have shown that even at high temperatures the presence of a trace of moisture is necessary for free oxidation (combustion), and that in *absolutely* dry oxygen, sulphur and phosphorus can be distilled, and carbon made red-hot without combustion taking place. A jet of burning dry carbon monoxide is even extinguished when introduced into pure and absolutely dry oxygen. The presence of the minutest trace of moisture is, however, sufficient to restore to oxygen its activity.

In ordinarily dry oxygen all substances which burn in air burn with much greater brilliancy, and many substances which do not burn in air burn vividly in oxygen. Thus iron, zinc, &c., if the ignition is started by a portion being raised to a white heat in an atmosphere of oxygen, continue to burn with great brilliancy and with the evolution of a very high temperature. The actual amount of heat given out during the complete oxidation of any substance is the same whether the combustion is slow or rapid, and is carried on in air or in oxygen. But it is quite different in regard to the temperature developed, this depending on the concentration of the heat, and so being higher the more rapid the combustion and the less extraneous matter is present to absorb the heat. Thus, when phosphorus is burned in oxygen, the temperature produced is very high, and the combustion takes place with dazzling brilliancy. The temperature of a hydrogen or a coal-gas flame burning in oxygen is very much higher than that of a similar flame burning in air. The temperature of a flame of hydrogen burning in oxygen is  $2800^{\circ}$ ; of carbon monoxide  $2600^{\circ}$ ; and of acetylene  $3000^{\circ}$ . These facts have been utilised in the construction of the oxy-hydrogen and oxy-acetylene blow-pipes for obtaining very high temperatures (*v. infra*). If coal-gas is substituted for the hydrogen, a very hot flame is still obtained, but the temperature is not as great as when hydrogen is employed. 16 grms. of oxygen combining with hydrogen to form water evolve 68,400 cal.

Oxygen is the only gas capable of supporting respiration, and forms the *constituent* of air. In the pure state it is inhaled for a time with impunity, and acts as a mild tonic or exhilarant. But its long-continued respiration is harmful, feverishness and weakness being produced; and it becomes poisonous if breathed under pressure. Dr. Richardson kept a rabbit in an atmosphere of pure oxygen at a temperature of  $23.9^{\circ}$  for 3 weeks. It lived all the time, but became so unable to assimilate new material fast enough to supply waste that it was found necessary to discontinue the experiment. At  $7.2^{\circ}$  the rabbit became speedily narcotised, and would have died had it not been removed. Richardson found that cold-blooded animals were very little affected by being introduced into an atmosphere of oxygen, whilst most warm-blooded animals (dogs, cats, guinea-pigs,

&c., but not the rat) showed no strong febrile symptoms. Some observers have noticed very decided narcotic effects produced in animals under these conditions, but Richardson ascertained that this is due to the oxygen becoming vitiated by repeated inhalations. He found that when the same oxygen was used over and over again, although purified from carbonic acid, &c., by passage over caustic potash, sulphuric acid, &c., the animals became speedily narcotised, but that when a continuous stream of fresh oxygen was employed this was not the case. This 'devitalising' of the oxygen appears to be due to traces in the exhaled gases of some compound which is not removed by the ordinary methods of purification. The electric discharge very quickly re-vitalised the vitiated oxygen. Flesh was found to decompose more readily in devitalised than in pure oxygen. At low temperatures, and at very high ones, however, oxygen is decidedly narcotic in its effect.

But although in health the continued inhalation of nearly pure oxygen is detrimental, its use where the action of the lungs and heart is sluggish, as in cases of partial suffocation, of collapse in cholera, pneumonia, and other illnesses, is very valuable, and has been the means of saving many lives. Its use in cases of cyanosis, gout, diabetes, &c., has also been found advantageous. Wounds and sores are said to heal more rapidly in an atmosphere of oxygen than in air, and it has been largely used in this connection.

*Methods of testing and estimation.*—The readiest test of moderate quantities of wood, a property only possessed by one other gas—viz. nitrous oxide. When mixed with colourless nitric oxide gas, oxygen produces deep reddish-brown fumes of nitric peroxide, whilst nitrous oxide does not. Nitrous oxide is also much more soluble in water than oxygen.

White indigo absorbs oxygen rapidly, at the same time turning blue. For general purposes of estimation, however, one of the three following methods is used:—

1. A solution of cupric chloride in hydrochloric acid (which is colourless) absorbs oxygen readily with formation of cupric oxy-chloride. The greenish-brown solution of this salt may be again reduced by keeping copper foil in it.

2. An alkaline solution of pyrogallol absorbs oxygen freely, forming a dark-brown liquid. Good results are obtained by mixing 45 c.c. of a 25 p.c. solution of pyrogallol (prepared by dissolving 60 grms. in 180 c.c. water) with 145 c.c. of 60 p.c. solution of caustic potash (prepared by dissolving 60 grms. ordinary stick potash in 100 c.c. water). 200 c.c. of this solution will absorb nearly two litres of oxygen, but it is better not to push the absorption beyond about 450 c.c. as then more or less carbon monoxide may be formed. Carbon monoxide is also sometimes formed when the percentage of oxygen in the gas being tested exceeds about 30 per cent. Clowes (J. Soc. Chem. Ind. 15, 170, 742) recommends the use of a very large excess of potash to prevent the formation of carbon monoxide. He advises 160 grms. potash dissolved in 130 c.c.

water, and 10 grms. pyrogallol added to the alkaline liquid.

3. Clean moist copper absorbs oxygen freely, but a skin of sub-oxide is rapidly formed over the copper, which prevents further oxidation. An ammoniacal solution of ammonium carbonate, however, readily dissolves this sub-oxide again, leaving the clean copper. To utilise this reaction for analysis a suitable absorption vessel is packed with fine copper wire and then filled with a solution composed of equal volumes of ammonia of sp.gr. 0.930, and of a saturated solution of commercial ammonium carbonate. When the gas in which the oxygen is to be estimated is introduced into the vessel and displaces the liquid, a large surface of clean copper is exposed, and the oxygen is rapidly absorbed. When the residual gas is removed, the liquid again fills the vessel and dissolves the sub-oxide of copper formed, leaving the copper clean for the next analysis. 200 c.c. of this solution will dissolve the oxide formed by the absorption of about 4 litres of oxygen, but it is advisable to renew it after the absorption of about 3 litres, as otherwise a good deal of a yellowish-brown precipitate (probably an ammonia-copper compound) forms which renders the renewal more troublesome. A little fresh copper wire must be occasionally added as that in the vessel gets used up.

For all these tests Hempel's, Orsat's, or Stead's apparatus (see ANALYSIS) answer well for all but the most delicate determinations. With these an oxygen determination can easily be made in 10 mins.

If the first method is employed, the gas after absorption must be freed from hydrochloric acid by means of potash.

The property of phosphorus of absorbing oxygen at ordinary temperatures is also sometimes used for analytical purposes, but this is not a generally convenient method. A hydrochloric acid solution of chromous chloride or an alkaline solution of ferrous tartrate may also be employed.

*Applications of oxygen.*—Oxygen has been used to maintain the air in a room in places where it cannot be replaced, as in diving-bells, submarine vessels, &c. Its use has often been suggested in connection with the ventilation of large halls, theatres, &c., but the cost has hitherto proved too great for its adoption.

It is employed in conjunction with hydrogen or coal-gas to produce the oxy-hydrogen and oxy-coal-gas flames in which platinum can be melted, silver distilled, &c. One application of these flames is in the production of the Drummond or lime light where the intense heat of the flame is made use of to raise a lime cylinder to a white heat and thus obtain an intensely vivid source of light. The oxy-hydrogen and oxy-coal-gas blowpipe is also used for the brazing of metals, autogenous soldering, the blowing and manipulation of hard-glass apparatus, and for many other purposes where very high temperatures and local heating are required (*v. also infra*).

Oxygen is used for many purposes in the laboratory, and, as already mentioned, for some medical purposes. It is found that the rate of respiration is increased (up to 6 or 7 p.c.)

of oxygen with nitrous oxide during anaesthetising with that substance prevents or reduces the tendency to convulsions experienced with pure nitrous oxide, without reducing appreciably its anaesthetic power. Johnson has shown (*J. pr. Chem.* [i.] 49, 148) that anaesthesia may be produced with nitrogen equally as well as with nitrous oxide, and that a mixture of nitrogen with 5-7 p.c. oxygen forms a very satisfactory anaesthetic, producing slight or no convulsions.

Oxygen has been applied in the purification of coal-gas from sulphur compounds. It is found that if from 0.5-1 p.c. of oxygen is added to the crude coal-gas before it enters the purifiers the reduction of the sulphur compounds to 8-12 grs. per 100 cubic feet of gas may be effected by lime alone, the use of oxide of iron or lime sulphide being unnecessary. If oxide of iron is used, its efficiency is increased. In any case the purifying space needed is lessened, the life of the purifying material is lengthened, and the luminosity of the purified gas is considerably increased. If lime is used for purification the fouled lime ('blue billy') has not the objectionable odour which it usually possesses (Valon, *Trans. Gas. Inst.* 1889, 41).

It has been found that if, during the bleaching of paper pulps and other materials with chlorine, the chlorine is given in a fine state of division, the bleaching potchee, a great saving of bleaching powder is effected, the bleached fibre also being stronger in texture (Thorne, *J. Soc. Chem. Ind.* 1889, 83).

Pure oxygen is also advantageously employed in the oxidation and thickening of oils for varnish and linoleum purposes. The thickened oil is paler in colour than boiled oil, the danger is less, as only steam heat is needed, and the thickening, besides being much more rapid, is accompanied by increase of weight instead of by loss of weight as in the ordinary process of boiling. The use of driers is also unnecessary (*Eng. Pat.* 18628, 1889).

Oxygen is now sometimes used to hasten the maturing of spirits, the same effect being produced in a few hours or days by means of pure oxygen acting on the spirit in a finely divided state as occurs under the ordinary method of storage in casks in 2 or 3 years.

Proposals have been made to use a mixture of oil gas and oxygen as an illuminating gas (Tatham, *Eng. Pats.* 13763, 16138, and 16142, 1889). It was found that, if 15-30 p.c. of oxygen is added to an oil gas retorted at a low temperature from a heavy and crude petroleum, a gas of very high illuminating power and of good travelling properties is obtained. The gas is a perfectly safe gas, as about its own volume of oxygen must be added to a heavy oil gas before an explosive mixture is formed. The same inventor proposed (*l.c.*) to use carburetted oxygen as a motive gas for engines, &c. He claims that with properly constructed valves, &c., perfect safety is secured, and that the great expansive force of carburetted oxygen on ignition gives results far superior to those obtained in the ordinary steam or gas engine.

The use in the manufacture of vinegar of small quantities of oxygen to act as a stimulant on the mycoderma has been found to considerably increase the rate of acetification.

L. T. T.

### THE PRODUCTION OF OXYGEN BY THE LIQUEFACTION OF AIR.

Since 1902, the liquid air process for the production of oxygen has rapidly come to the front and with the single exception of the electrolytic method it is now the oxygen process almost exclusively employed for commercial purposes.

The separation of liquid air into its main constituents, oxygen and nitrogen, was a problem which for many years, prior to 1902, occupied the attention of physicists and chemists who have studied the practical production of extreme cold and the liquefaction of gases.

It was, however, not until 1895 that the first real step of importance was taken in the practical production of liquid air. In that year, Carl von Linde took out a patent (Eng. Pat. 12528, 1895) for an apparatus which marked a new era in the production of liquid air and a serious step in the separation

It had been proved by Thomson (Lord Kelvin) and Joule that if compressed air were allowed to expand without doing external work there was a slight fall of temperature due to the fact that internal work must be done in such expansion. Linde first realised<sup>1</sup> that this cooling effect increased very rapidly as the temperature fell, and in his patent of 1895 he utilised the fact to make a most practical and effective air-liquefier. He took highly compressed air at ordinary atmospheric temperature and caused it to pass through a coiled copper pipe contained in a well insulated heat inter-changer, so constructed that the air which was allowed to expand through a throttle valve at the lower end of the coil was then caused to pass back in a reversed flow through the inter-changer in intimate contact with the external surface of the pipe, through which the compressed air was passing on its way to the expansion valve. The principle of regenerative cooling was thus established between the expanded and compressed air with a self-intensive cooling effect which continued to increase until the cold became so great that a portion of the incoming compressed air was liquefied and collected in the vessel. Linde employed no preliminary cooling of the air and by this simple construction of self-intensive counter-current interchanger, there is no doubt that he originated an apparatus of much scientific value and perhaps of much direct

patent, Linde did not aim merely at providing a simple method of producing liquid air: his real object was by liquefaction and subsequent fractional evaporation to separate its constituents in order to obtain

oxygen of commercial purity. To do this, Linde relied on the fact that nitrogen being more volatile than oxygen the vapour from a liquid mixture of the two was richer in nitrogen than was the liquid itself. This process of fractional evaporation did not, however, prove successful. It was found by experiment that under the most favourable conditions in order to obtain a residue containing 50 p.c. of oxygen 70 p.c. of the liquid had to be evaporated, and that the further evaporation was carried the greater became the proportion of oxygen lost in the vapours. Thus in the end when the liquid approached the ordinary commercial standard of purity in oxygen its quantity had become so minute as to be practically valueless.

The following table, prepared by Linde from his own experiments, clearly shows how the composition of the liquid changes even under the most favourable conditions, viz. during slow or quiet evaporation.

Per cent. of liquid not yet evaporated.	Per cent. of oxygen in liquid.	Per cent. of oxygen in vapour coming off.	Per cent. of original oxygen still in liquid.
100.0	23.1	7.5	100.0
50.0	37.5	15.0	80.0
30.0	50.0	23.0	65.0
20.0	60.0	34.0	52.0
15.0	67.5	42.0	43.0
10.0	77.0	52.0	33.0
5.0	88.0	70.0	19.0

Between 1895 and 1902, many patents were taken out for the production of liquid air, and the separation of its constituents. Nearly all appear to derive their inspiration from Linde, the low temperature for liquefaction of the air being obtained in practically every case by his nozzle expansion self-intensive system, whilst fractional evaporation of the liquid was invariably the system employed for obtaining oxygen.

As a matter of historical accuracy it must be admitted that for the seven years following Linde's patent of 1895 no substantial progress was made towards the industrial separation of oxygen from liquid air. It was not until 1902 (Eng. Pat. 14111, 1902) that Linde himself took the final step which solved that problem and laid the foundation for what is to-day undoubtedly the cheapest and best process for the production of oxygen.

It has already been shown that to obtain oxygen from liquid air by fractional evaporation a serious loss was entailed of the very substance that the process was designed to produce. It was this difficulty which Linde solved in his patent of 1902 and he accomplished it by adapting to the treatment of liquid air the process of rectification long known and employed in the production of alcohol (see ALCOHOL). Linde himself regarded his 1902 invention solely as an addition to the method of obtaining oxygen from liquid air by means of fractional evaporation as described in his 1895 patent and he only claims it as such. By introducing a rectification column, however, on the top of his evaporation chamber he not only succeeded in

<sup>1</sup> It is a coincidence in the history of invention that the Eng. Pat. 10165 of 1895 was applied for by an Englishman, Dr. William Hampson, a few weeks before Professor Carl von Linde took out his British Patent. Hampson's patent is held by some to anticipate Linde in this country although there is no question as to the priority of Linde elsewhere. The terms of Hampson's provisional specification are somewhat ambiguous and it is difficult to say how much credit should be attached to this publication. Full details of Linde's apparatus were made known before the completion of Hampson's patent so that unfortunately his claim to priority has to stand on his provisional specification alone.

arresting the oxygen which was formerly lost but actually employed it to form part of a continuous rectification process for the production of oxygen in a state of remarkable purity.

The simplest form of the Linde Oxygen Separator as employed to-day embodies all the essential features of his 1902 patent, so that a brief description of the actual machine with special reference to the accompanying diagrams may be taken as describing all the important characteristics of the apparatus as set forth in the specification and claim of that patent.

Fig. 1 represents diagrammatically the sectional elevation of a Linde separator capable of producing large quantities of oxygen of 80 to 90 per cent purity. The circular upper portion of the apparatus is made of wood, contains in its interior a vertical column A, whilst the base is constructed in the form of a hexagon

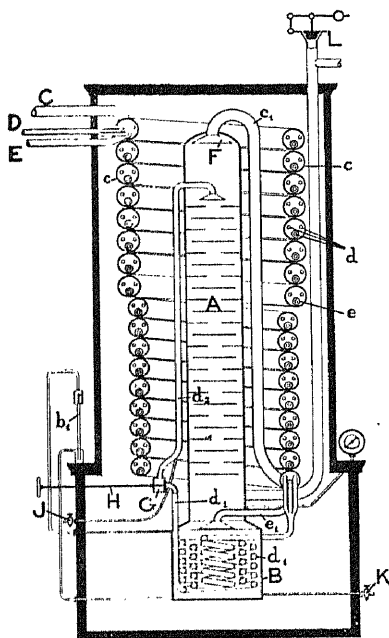


FIG. 1.

contains the vapourising, or distilling chamber B. All clearance spaces are packed with sheep's wool or other suitable insulating material in order to prevent the penetration of heat from outside sources. *c* is the counter-current interchanger constructed in the form of a large copper spiral pipe and containing three small copper pipes *d*, one of which is enclosed in a larger pipe *e*, as indicated more clearly in the sectional diagram, Fig. 2. *c*<sub>1</sub> is an extension of the main spiral pipe to the top of the rectifying column A with a gas or vapour collecting funnel *f* projecting within the same. *e*<sub>1</sub> is an open funnel-ended extension of the pipe *c* at the top of the vapourising chamber B. The pipe coil *d*<sub>1</sub>, shown in Fig. 2, is connected at one extremity with the small pipes *d*, contained in the counter-current interchanger. The other extremity of this pipe is connected

with the inlet of the valve box *a*, to the outlet of which another pipe *d*<sub>2</sub> is connected as shown. This pipe is carried upwards and enters the rectification column near the top where it is fitted as shown with a rose end, the function of which will be explained later.

With this preliminary description of the essential parts, the working of the apparatus can now be readily followed. There are two stages in the working.

First, the preliminary cooling down and production of liquid, and second, the separation of oxygen from the liquid.

In commencing to work the machine, air at normal atmospheric temperature, or less, and at a pressure of about 2000 lbs. per sq. in. is conveyed from a gas compressor of suitable construction through the main pipe *D*, into the three small pipes *d* of the counter-current interchanger. It passes down these pipes to the pipe coil *d*<sub>1</sub> in the vapourising chamber *B*. At this point, by the adjustment of the regulating valve spindle *x*, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose ended pipe *d*<sub>2</sub> into the top of the rectification column. This expanded air fills the column and then flows through the only two possible outlets, *c* and *e*, into the counter-current interchanger, in a reverse flow to the incoming high pressure air, leaving the apparatus through the pipes *c* and *e* as indicated.

It is at the valve *a* that Linde obtains the Thomson-Joule effect to which reference has already been made and regenerative cooling occurs in the counter-current interchanger where the incoming compressed air parts with some of its heat to the expanded air which has been rendered colder by its own drop on expansion. The whole apparatus goes on until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vapouriser *B*. The quantity of liquid thus collecting is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube *b*<sub>1</sub> enclosed in a pressure equalising circuit as indicated.

When the whole apparatus has been cooled down nearly to the temperature of liquid air, the liquid begins to accumulate rapidly in the vapouriser *B*, and the initial pressure of the air may be gradually reduced by increasing the opening of the valve *a*. Until this stage is reached, any separation of oxygen and nitrogen, which may have occurred, has been due simply to fractional evaporation.

As, however, the liquid begins to accumulate round the coil in the vapouriser *B*, the compressed air transmits some of its latent heat to the liquid. The latter is thereby evaporated

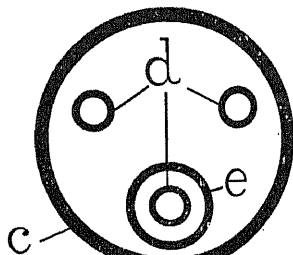


FIG. 2.

whilst the compressed air is itself liquefied in proportion to the amount of heat thus extracted. The vapours thus produced begin to flow upwards through the rectification column in which the liquid air is flowing downwards. The temperature gradient necessary for efficient rectification then rapidly becomes established in the column and the second stage is reached in which the apparatus can be employed for the production of oxygen.

In the separation of oxygen from liquid air by rectification, Linde relies for his temperature gradient on the difference between the boiling-points of nitrogen and oxygen. The former is  $77.5^{\circ}$  absolute and the latter  $91.5^{\circ}$  absolute. Liquid air is discharged into the top of the column at a temperature of about  $81^{\circ}$  absolute. Nitrogen being the more volatile component it immediately begins to boil off, and thus automatically creates the maximum cold at the top of the column. For the same reason the nitrogen present in the original liquid collected in the vapouriser is the first element to be liberated by latent heat from the compressed air, so that the temperature of the liquid in the vapouriser becomes higher as its content of nitrogen increases, thus the highest temperature is :

automatically at the bottom of the column. When all the nitrogen has been expelled from the vapouriser, liquid air passing down the column over various baffle plates comes into intimate contact with rising vapours of oxygen and an exchange of material takes place. At each stage some of the rising oxygen is condensed and some of the nitrogen in the down-coming liquid is evaporated whilst the liquid gradually gains in temperature until by the time it reaches the vapouriser its composition is that of practically pure oxygen. The gas, on the other hand, which passes off from the top of the column through the funnel *r* and the pipe *c*, to the counter-current interchanger, *c*, is mainly nitrogen at a temperature about  $14^{\circ}$  lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column to effect the material exchange with the nitrogen of the liquid air is carried back to the vapouriser together with most of the oxygen contained in the original liquid. The excess of oxygen which thus continually gathers at the bottom of the apparatus is drawn off in a gaseous condition through the pipe *e*, into the pipe *e* of the counter-current interchanger. It will thus be seen that the gases drawn from the top and bottom of the apparatus are made to abstract heat completely from the incoming compressed air which is on its way to be liquefied.

The pressure at which the cold gases escape from the apparatus is from 4 to 5 lbs. per sq. in., just enough to cause them to pass freely through the counter-current interchanger. *L* is an emergency release valve on the low pressure system. *J* and *K* are test cocks communicating with the liquid air and liquid oxygen supplies respectively.

After the regular condition of oxygen producing has been reached the apparatus works steadily, the air supply from the compressor being kept at sufficient pressure not only to ensure its liquefaction at the temperature of the liquid oxygen bath (say  $91^{\circ}$  absolute), but

also to ensure that the drop to the low pressure of from 4 to 5 lbs. sq. in. is sufficient to make good thermal losses due to leakage of heat from outside and to imperfect interchange in the counter-current apparatus. In practice, this pressure is found to be from 50 to 60 atmospheres.

A separate fore-cooler for the compressed air (not shown) is usually employed with the Linde apparatus. This fore-cooler is kept cold by means of a carbonic acid or an ammonia machine and is interposed between the air compressor and the separator so that the air leaving the compressor at normal atmospheric temperature becomes reduced to a temperature well below the freezing-point of water before it enters the separator. By this means, practically all the moisture which has not previously been abstracted by compression gets frozen out of the air. This is a point of more importance in actual work than the slight supplementary cooling which is obtained, because unless the air is thoroughly dry before it enters the coils of the counter-current interchanger the working of the apparatus is liable to be interrupted by the formation of ice which has to be thawed out before work can be resumed. This is an operation which involves considerable delay. It is usual therefore to make both fore-coolers and separators in duplicate to ensure continuous working. In addition to the elimination of moisture it is also desirable to remove carbonic acid from the air. This is usually done by drawing the air on its way to the compressor through a purifier containing caustic soda. In practice, separators work for a week or longer without freezing up and fore-coolers for about two days.

The three essentials of Linde's process could not be more concisely or accurately described than in his own patent specification. They are (1) cooling the air to be condensed in causing it to flow in the contrary direction to the evaporating products; (2) in then causing the same to transmit its latent heat to the evaporating liquid, and (3) in then causing the vapours produced in the distilling apparatus to flow upwards through the liquid flowing downwards in a stratified manner.

The first condition established the economy of the process by using the cold separated gases passing out of the apparatus to abstract heat from the incoming compressed air. It was by realising the second condition that Linde was able to achieve perfect rectification. Although the already cold compressed air is made to part with its latent heat while liquefying in the coils of the distilling apparatus its actual temperature cannot exceed that of the oxygen vapour which it has produced. By taking this liquid to the top of the column and letting it escape from a high to a low pressure the portion thus escaping undergoes an instantaneous partial volatilisation which, as already explained, reduces it so much in temperature that it can play the part of the cold member of the combination and thus establish the correct temperature gradient for the material exchange between liquid and vapour which the process renders possible.

The action which takes place in Linde's rectification column can be readily understood

by reference to Baly's experiments on the 'Distillation of liquid air and the composition of the gaseous and liquid phases at constant pressure,' published in 1900 (Baly, Phil. Mag. 1900, 49, 517). It has already been shown (table, p. 45) how the composition of the liquid air changes during slow evaporation. Baly's experiments show that given any liquid mixture of oxygen and nitrogen equilibrium between its liquid and vapour is possible only where the vapour contains a definite proportion of the two constituents, but this proportion is not the same as that in the liquid.

The results in this direction obtained by Baly in a series of experiments are graphically set out in the diagram, Fig. 3, in which the ordinates indicate temperatures and the abscissæ percentages of oxygen. The curves

indicate the composition of liquid and vapour respectively at definite temperatures. From these curves it will be seen that with vapours and liquid in equilibrium the vapours are always richer in nitrogen than their liquid. Thus when the evaporating liquid is liquid air (oxygen 21 p.c., nitrogen 79 p.c.), the proportion of oxygen present in the vapour coming off must be not less than 7 p.c. Although it is therefore possible by simple rectification as employed in Linde's apparatus to expel all nitrogen from the liquid by material exchange with the oxygen vapours, nitrogen itself can never contain less than 7 p.c. of oxygen. Whilst, therefore, the apparatus is capable of producing—and does produce—pure oxygen it is impossible to obtain nitrogen of equal purity without further treatment (see NITROGEN).

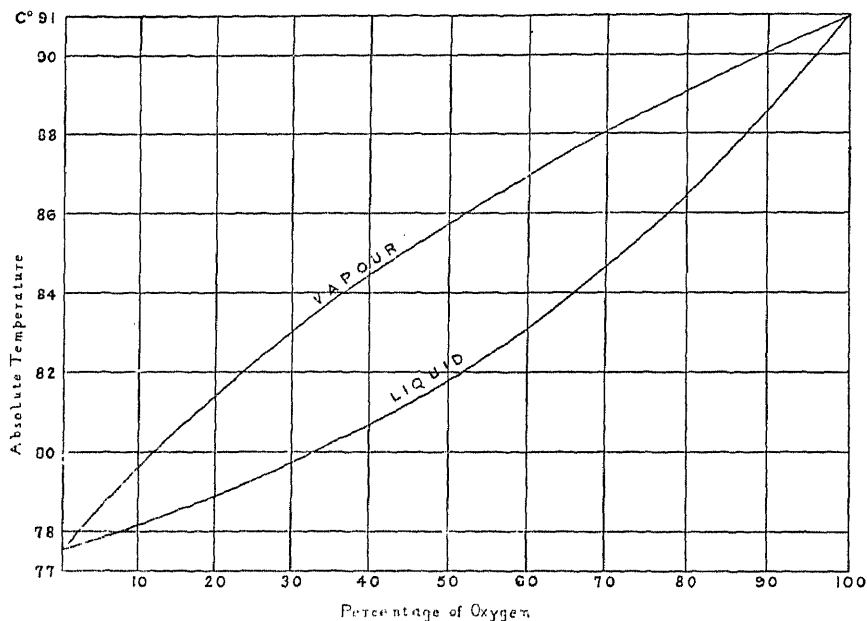


FIG. 3.

With the correct temperature gradient of the Linde rectification column it is easy to apply the conditions of the Baly curves. Starting with liquid air at the top of the column we know that 7 p.c. of oxygen must be present in the vapour given off. As the liquid descends it comes in contact with gas containing at each stage more oxygen than corresponds to conditions of equilibrium. Accordingly, oxygen is continually being condensed and nitrogen evaporated in the effort of the liquid to establish a condition of equilibrium with a vapour of constantly changing partial pressures, until ultimately at the base of the column pure oxygen is obtained.

Rectification, according to Linde's invention of 1902, although it yields pure oxygen, cannot be regarded as complete because, as explained, it leaves not less than 7 p.c. of oxygen in the waste gas.

A comparatively simple modification of the

Linde process enables separation to be carried a stage further. This improvement is due to M. Georges Claude. Instead of condensing the compressed air integrally and then discharging it in one stream at the top of the rectification column, Claude employs a fractional method of liquefaction which separates the air on condensation into two liquids, one containing an excess of oxygen and the other an excess of nitrogen. The rectification column is made higher than that of Linde, and the liquid rich in nitrogen is discharged from the top, whilst the liquid rich in oxygen enters the column at a lower point appropriate to the proportion it contains of the two constituents. The additional scrubbing thus obtained with a liquid richer in nitrogen than air is the means of arresting a further 3 p.c. of oxygen without any additional expenditure of power. The waste gas consequently leaves the Claude apparatus with an oxygen content of only 4 p.c. Although

Claude's apparatus is somewhat more complicated to operate than that of Linde and requires more constant supervision, there is no doubt that this ingenious addition to the Linde process is of some practical value where large installations are concerned.

It may be mentioned here that this process has not been found possible by the Linde process to separate completely the components of liquid air so as to collect both the oxygen and nitrogen in a state of purity, but by pushing Claude's system of fractionation a stage further to obtain small quantities of pure oxygen in an oxygen separator. This process, requiring any additional power, by a further fractionation of the liquid already rich in nitrogen. About 10 p.c. of the total nitrogen can thus, if desired, be obtained in a condition of purity the vapours being separately drawn off through the counter-current interchanger to a nitrogen holder. As the abstraction of this pure nitrogen from the liquid involves a somewhat higher percentage of oxygen in the rich nitrogen liquid supplied to the top of Claude's rectification column, it is obvious that the waste gas must also contain a somewhat higher percentage of oxygen, so that whilst pure nitrogen is being abstracted the normal yield of pure oxygen is appreciably diminished. The device is, however, a simple one which does not in any way impair the working of the separator when oxygen alone is required and as there is a small but growing demand for nitrogen in cylinders it is a profitable addition to the ordinary separator of an oxygen factory.

In the economical development of Linde's process, Claude is entitled to the further credit of being the first to utilise part of the energy contained in the compressed air by expanding it in a cylinder to perform external work. He thus obtains a greater degree of cooling than when Linde's system of nozzle expansion alone is employed.

Claude takes air from the compressor at a pressure of from 25 to 35 atmospheres, and after cooling it in the counter-current interchanger he expands it in the cylinder of his expansion engine to a pressure of 4 to 5 atmospheres. It then enters the separator where fractionation, liquefaction and ultimate rectification take place as already described. The power developed by the expansion engine can be absorbed in driving a dynamo or in any other suitable way, but the amount of energy recovered is so small that as an economy in the production of oxygen can be entirely disregarded. On the other hand, the fact that Claude can use air at an initial pressure of from 25 to 35 atmospheres as compared with Linde's pressure of 50 to 60 atmospheres indicates a total saving about 20 p.c. in power. In small plants (say up to a production of 20,000 cubic ft. of oxygen per 24 hours) this economy is probably quite counterbalanced by the additional complication and supervision involved. On the other hand, like Claude's addition to Linde's separator, his expansion engine becomes of practical value where large installations are concerned.

The Linde British patents were acquired in 1906 by the British Oxygen Company, Ltd., a  
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concern which was founded as Brins Oxygen Company, Ltd., in 1886 (*v. infra*). From the end of 1907 until March, 1909, the Linde rectification patent and important litigation was unanimously upheld both in the Court of Appeal and the House of Lords.

The British Oxygen Company possess oxygen factories in London (2), Birmingham, Cardiff, Manchester, Sheffield, Newcastle-on-Tyne, and Glasgow. All of these are equipped with liquid air plants, including two on the Claude system (Claude's patents of addition having also been acquired by the Company). The total capacity of all the Company's oxygen plants at the present time (1913) is 400,000 cub. ft. per day of 24 hours, the quality of oxygen being as high as 99 p.c.

The cost of production varies considerably with the size of the plant. A plant to produce 40,000 cub. ft. of oxygen per 24 hours (which is a common size at the present time for a single unit in an oxygen factory) involves, in power, a total expenditure of about 100 h.p. Taking this at 0.35d. per h.p. hour, and adding all other direct charges, except depreciation and interest on capital, the cost per 1000 cub. ft. of oxygen into the holder works out at about 3s. 6d. The cost of such a plant complete with motive power, gas holder, and erection is approximately £7,500.

#### THE PRODUCTION OF OXYGEN BY THE ELECTROLYSIS OF WATER.

With the steady reduction in the cost of electrical power which has taken place in recent years combined with improvements in electrolytic apparatus, the production of oxygen and hydrogen from water by electrolysis has undoubtedly been established on a commercial basis.

Of the various processes employed to-day, the best known are probably those of Garuti, Schneckert, and Schmidt.

In all apparatus for the electrolysis of water, two essential conditions have to be observed:—

*First:* Reduction to a minimum of the electrical power required.

*Second:* Perfect separation of the two gases.

Water itself, as an electrolyte, is a poor conductor. It is usual therefore in all cases to render the liquid alkaline by the addition of 15 p.c. caustic soda or 20 p.c. caustic potash in order to improve its conductivity and thus facilitate the reaction.

The separation of the two gases depends largely on the construction and arrangement of the electrodes and diaphragms, or partitions, employed in the voltimeters, or electrolyzers, as they are more commonly termed, and it is principally in this respect that the various forms differ. Where diaphragms are employed, they should be permeable to the electrolytic solution, impermeable to the gases evolved, and they should be good conductors. Many porous materials, such as porcelain, pipe-clay, asbestos, plates of carbon, &c., have been employed, but all appear to have failed to realise satisfactorily one or the other of the requisites mentioned.

The objection at first to the use of metallic diaphragms was that they came under the



influence of the electric current by induction from the electrodes. They thus acted to some extent as bi-pole electrodes, thereby creating a tendency for the two gases to be liberated in the same compartment, or cell.

Garuti discovered that if the electromotive force did not exceed 3 volts, and if the current was under 2 ampères per square decimeter of electrode, a metallic diaphragm remained passive, and he found that owing to its feeble resistance it was possible to work the apparatus

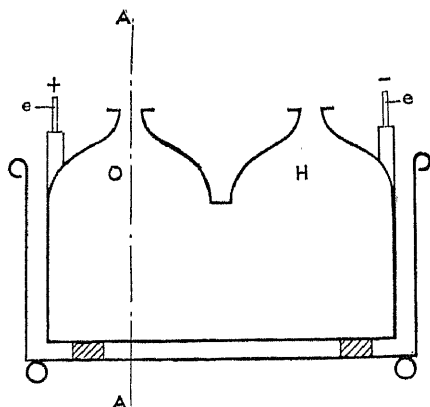


FIG. 4.

with a difference of potential well under 3 volts. Garuti discovered, however, that it was necessary to carry the bottom of the diaphragm below the level of the bottom of the electrodes in the electrolyser in order to ensure this passive condition, and that this construction prevented

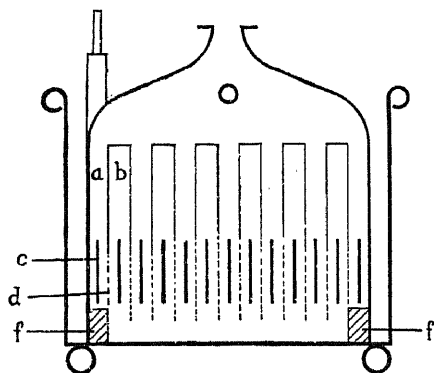


FIG. 5.

good circulation of the electrolyte. He overcame the difficulty by perforating a large number of minute holes in the lower or immersed portion of the diaphragm. Whilst these holes permit the electrolyte to circulate they are practically impermeable to the gases.

Figs. 4 and 5 illustrate diagrammatically a side elevation and cross section through  $\Delta\Delta$  of a Garuti electrolyser of this description. The outer tank in each is shown cut away.

The apparatus is composed of a series of

alternate sheet steel compartments, or cells,  $a\ b$ , each enclosing an electrode  $c$  and consisting of long diaphragms  $d$  welded on to end plates and built up side by side. They are completely open at the bottom and the lower portion of the diaphragm is perforated as indicated. They are all open at the top for half their length, those containing an anode, or positive electrode (viz.  $a$ ), being open to the left half of the figure and those containing a cathode, or negative electrode (viz.  $b$ ), to the right half of the figure. In this way the left half of the cover welded on to the left; whilst the oxygen from the cells  $a$ , whilst the corresponding bell welded on to right portion  $H$  collects hydrogen from the cells  $b$ .

The anodes on one side and the cathodes on the other are welded to terminals  $e$  for the transmission inwards and outwards of the current. When the electrolyzers are large the diaphragms and the electrodes are maintained rigid and equidistant by means of wooden partitions, or combs  $f$  placed at the lower extremity as indicated.

In the Schuckert electrolyser, the separation is effected with the aid of a metallic partition, or screen, between the electrodes, each of the latter being metallically suspended from the centre of a gas collecting bell which seats itself in the electrolyte so that the

each electrode can be separated by a screen which is insulated from the metallic bells is carried into the electrolyte so far below the edges of the bells that the anodes and cathodes, that the bells are practically unaffected by the current lines set up in the electrolyte. On the other hand, the bottom edge of each electrode is carried so far below the bottom edge of the screen that the gases generated at the respective electrodes can be obtained in a pure condition. The bells containing the electrodes and also the screens are independently constructed and may be multiplied in one electrolyser as desired.

Both the foregoing types of electrolyzers, which indicate the general construction of such apparatus, work without any special supervision. They are usually made to produce from one half to two cubic metres of oxygen per hour and consequently that quantity of hydrogen. The electrolyzers are placed in batteries side by side in a room which must be provided with excellent ventilation, or a ventilating fan, chiefly in order to obviate all risks through leakage, of explosive mixtures of the gases. In order to attain its full capacity the temperature of the electrolyte should be from  $50^{\circ}$  to  $60^{\circ}$ . The temperature of the room containing the electrolyzers is therefore apt to become excessive unless adequate ventilation is produced. The requisite heat is generated and maintained in the electrolyte by its own decomposition, but steam heating is frequently provided and particularly when the electrolytic apparatus is arranged to work intermittently.

The gases produced under normal working conditions in a good electrolyser have the following degree of purity:—

Oxygen, 95–97 p.c.

Hydrogen, 97–99 p.c.

The impurities are mainly oxygen and hydrogen respectively and these residuals are

largely eliminated . . . . . uses through tubes containing . . . . . purmice on their way from the electrolyzers to their respective holders. In the heated tube, the impurity in each case combines with some of the major gas in the form of steam, which is removed by condensation.

The first cost of a Schuckert electrolyser to produce  $\frac{1}{2}$  cubic metre of oxygen and 1 cubic metre of hydrogen per hour is given as about £75. Consequently for a plant to produce about 40,000 cubic feet of oxygen per 24 hours, the electrolytic apparatus alone, assuming current to be taken from an existing private source, or public supply, exceeds the cost of a liquid air plant of the same capacity *with power included*. If the first cost of the current added to that of the electro-

that the complete electrolytic installation costs more than double that of liquid air. It should, however, be pointed out that in smaller plants this difference in first cost is not so marked, whilst hydrogen, as the electrolytic by-product, is at present a more valuable than the nitrogen of liquid air. Composing water by electrolysis into its components, oxygen is mainly a question of the . . . involved, and the consumption of energy under normal conditions can be readily calculated from existing data:—

One ampere decomposes 0.335664 grm. of water per hour, and liberates 0.037273 grm. of hydrogen and 0.29839 grm. of oxygen.

One litre of hydrogen weighs 0.0896 grm.

One litre of oxygen weighs 1.4300 grm.

Therefore in one hour an ampere liberates from water 0.416 litre hydrogen and 0.208 litre oxygen.

Calculated on Thomson's law, according to which the heat disengaged by the formation of water equals the E.M.F. necessary for its decomposition, it is found that 1.5 volts is the E.M.F. required. In practice, it is not possible to realise this theoretical result and it is admitted that an E.M.F. of not less than 2.5 volts is necessary.

of 208 litres of oxygen, latter voltage, gives  

$$\frac{0.208 \times 1000}{2.5} = 83.2 \text{ litres of oxygen per kilowatt hour.}$$
 Therefore, to obtain 1 cubic metre of oxygen and 2 cubic metres of hydrogen exactly, 12.0 kilowatt hours are required.

Schuckert gives the consumption of energy with his electrolytic system as 12 to 14 kilowatt hours per cubic metre of oxygen. The manager of a large factory in Germany, employing Garuti's process, recently gave the present writer the figure of 13.5 kilowatt hours as his experience, and 15 kilowatt hours has been given to the writer by other users of large electrolytic plant.

An average of 14 kilowatt hours (say) 20 B.H.P. hours, is consequently a reasonable estimate of power required in actual experience with large plants for the electrolytic production of one cubic metre of oxygen and two cubic metres of hydrogen.

An electrolytic plant of the capacity which has been considered in the case of liquid air, viz. an output of 40,000 cubic feet of oxygen

per 24 hours, requires therefore more than 9 times as much motive power as the corresponding liquid air plant. Assuming that current is drawn from a public supply at  $\frac{1}{2}$ d. per unit (a price at which it can be readily obtained to-day in many places), the cost of energy per 1000 cubic feet of oxygen is 16s. 8d. Allowing 2s. 4d. to cover other direct charges, such as wages, material, current losses, renewal of plates, &c., and assuming the same depreciation and interest on capital, then regarded as oxygen producing processes, the respective figures of 3s. 6d. and 19s. may be taken as a fairly accurate comparison of the cost of production.

It is obvious therefore, that unless a ready market can be found for hydrogen, the electrolytic process cannot at present compete on equal terms with liquid air plants in the oxygen factory.

#### INDUSTRIAL PRODUCTION AND USES OF OXYGEN.

Prior to Linde's invention of 1902, oxygen for industrial purposes was produced by electrolysis, except in this country where the Barium Oxide process was for many years successfully employed by the British Oxygen Company. The Barium Oxide process must to-day be regarded as obsolete because, in first cost, quality of oxygen produced and cost of production it is quite unable to compete with Linde's liquid air process.

The electrolytic process, on the other hand, can at least supply a gas of equal purity, and where a useful outlet can be found for hydrogen the process can probably hold its own—particularly in cases where small private plants are required to produce oxygen in the works where it is to be consumed.

Three circumstances have, however, conspired in recent years to arrest development in the use of electrolytic apparatus for the production of oxygen. The first is the established success of the Linde process. The second is the introduction of oxy-acetylene welding which has not only largely superseded the older method of oxy-hydrogen welding but has in consequence created an extensive demand for oxygen, *per se*, thus detracting largely from the value of the hydrogen product on which the success of the electrolytic process mainly depends. The third is the low price at which oxygen can now be obtained in cylinders. This tends to restrict the sale of apparatus for private manufacture of the gas.

The two most important industrial outlets for oxygen at present are oxy-acetylene welding and oxygen metal-cutting. Neither process has been before the public for more than six years, yet engineers have been quick to recognise the fact that each affords a valuable and economical method of dealing with an immense variety of metallurgical operations.

The increased demand for oxygen due to these developments has led to a very large increase in the number of oxygen factories.

In this country, besides the numerous extensions of the British Oxygen Company, to which reference has already been made, a number of electrolytic plants exist which produce oxygen either for private use or distribution in

cylinders. In Germany, France, and Belgium, six years ago, there existed altogether about twelve oxygen factories nearly all employing electrolytic plants. To-day that number has been quadrupled by liquid air plants alone and a considerable number has also been installed in France, Belgium, and Germany.

Every country in Europe, has now one or more oxygen factories, and it is no exaggeration to say that all important engineering centres have practically unlimited supplies of oxygen available, in fact, the supply at the present time considerably exceeds the demand.

The total consumption of oxygen in Germany in 1911 was 100,000,000 cubic feet. In France, it was about 100,000,000 cubic feet and in England about two-thirds that amount. 90 p.c. of the total consumption may safely be attributed—in about equal proportions—to welding and metal-cutting. The price of oxygen in cylinders for these industrial applications is about the same in each country and varies from  $\frac{1}{4}$ d. to  $\frac{3}{4}$ d. cubic foot, according to locality and the quantity purchased.

In the United States of America, development has been slower owing to the dearth of oxygen factories. Five of these are, however, now in operation, equipped with Linde plants, and at least two other factories exist for the electrolytic production of oxygen. The oxygen industry is therefore certain to expand rapidly in America during the next few years.

In order to complete the list, it may be added that Linde oxygen plants, for the development of oxy-acetylene welding and metal-cutting, have been recently erected, or are in course of erection in Australia, New Zealand, South Africa, Egypt, India, China, Japan, Brazil, and the Argentine.

*Oxy-acetylene welding.* The temperature of the flame in a good oxy-acetylene blowpipe is approximately  $3315^{\circ}$  ( $6000^{\circ}$ F.). This high temperature is mainly brought about by the combustion of carbon to carbon dioxide. Acetylene has a heating value of about 1500 B.T.U. per cubic foot. It is an endothermic gas approximately composed of 92.5 p.c. carbon and 7.5 p.c. hydrogen, which in combustion with oxygen form carbon dioxide and water. In consequence of the high flame temperature, however, the water formed by this primary combustion is dissociated into hydrogen and oxygen, the latter element combines at once in the flame with the carbon of the acetylene to form carbon dioxide, whilst the hydrogen can only combine with oxygen which has passed out of the hottest zone of the flame, and thus does not involve a consumption of heat at the expense of the hottest part. It is, in fact, claimed for oxy-acetylene welding that the hydrogen forms a relatively cool jacket round the hot flame produced by the combustion of carbon in oxygen, and that as the hydrogen is not able to combine with oxygen at the very high temperature which exists within the inner zone, but remains temporarily in a free state, it protects the inner zone in a measure from loss of heat, whilst largely excluding the tendency to oxidation of the metal—a defect from which all other methods of welding suffer.

Theoretically,  $2\frac{1}{2}$  volumes of oxygen are required for the complete combustion of 1

volume of acetylene. In practice, however, with the oxy-acetylene blowpipe, it is found that the best welding results are obtained with 1.5 volumes of oxygen to 1 volume of acetylene.

The strength of the weld produced by the flame is almost invariably somewhat less than that of the original material. This may often be due to the use of welding strips of inferior tensile strength. It is, however, undeniable that the structure of the material in the weld is less homogeneous than in other parts. A good weld is largely a matter of skill on the part of the individual welder. It is possible for a competent welder, at his own discretion, to give a greater or less strength to the welded part, and for this reason it is impossible to draw conclusions from the work of one man as to the work of another. Oxy-acetylene welding must be regarded as a trade which can only be mastered by intelligent work and gradual development from simple to difficult jobs. Much depends on the intelligence and ability of the workman. A skilful welder will use a hammer freely as well as a blowpipe, more especially on vertical or overhead welds in plates which are subsequently to be subjected to pressure strains. By the judicious use of hammering at the right moment on the welded part the metal can always be made denser, with the result that the strength of the weld is increased.

The oxy-acetylene system of blowpipe welding is employed in two forms, which may be described as the high and low-pressure systems.

The first to be introduced was the high-pressure system, in which both gases are delivered to the blowpipe under pressure. Oxygen is supplied from an ordinary trade cylinder, and acetylene from a cylinder in which it is dissolved in a porous material soaked in acetone. Acetone has the property of absorbing 25 times its own volume of acetylene at atmospheric pressure, and it continues to absorb it at a pressure of 150 atmospheres. This system affords an efficient method of transporting acetylene and it is used with the means of using a blowpipe in its most portable form for many useful applications, and for repair work generally, but more especially on board ship, this system is admirably adapted.

The low-pressure system is almost exclusively employed for welding purposes in engineering works. In this latter method, only oxygen is required from a cylinder. Acetylene may be taken from any ordinary generator of approved design.

Oxygen has to be supplied to the blowpipes at a constant low pressure of from 5 to 30 lbs. according to the size of blowpipe employed. For this purpose the high and varying pressure of the gas cylinder is reduced to the constant low pressure required, by means of a pressure regulator which is attached to the cylinder. Acetylene (which must be well purified) is conveyed by any suitable system of piping from the holder of the generator to the place where it is to be employed. The blowpipes used are invariably of the injector type in which the oxygen under a suitable pressure is made to draw the necessary quantity of acetylene into

the blowpipe and then deliver both gases well mixed and under sufficient pressure through the burner nozzle.

Fig. 6 illustrates a popular type of an injector blowpipe which, in addition to possessing all the usual characteristics of such a tool,

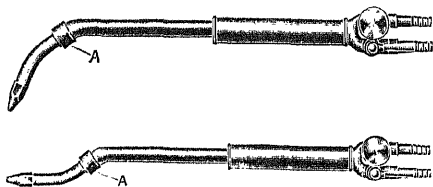


FIG. 6.

is fitted with a head which can be adjusted as indicated to suit any special conditions of work.

It is impossible to enumerate in detail all the work which may be executed by the oxy-acetylene blowpipe rapidly and economically, but the following are some of the applications for which it has already been advantageously employed:

The fusion welding of bicycle frames, forks, tee standards, wheel rims, &c.; the fusion welding of frames, wheel rims, &c., for motor cars; the repair of locomotive frames, &c.; in the manufacture of iron or steel motor or other boats as a substitute for rivets; the fusion welding of domestic and other hot-water boilers; the repair of steam boilers, boiler flues and other apparatus *in situ*; the fusion welding of steel or iron tanks, &c.; in the manufacture of safes; the fusion jointing of pipes of every description and shape for steam superheaters, &c.; the fusion welding of all joints in metallic castings, such as barrels, &c.; as a substitute for sheet metal, such as enamel ware; artistic ironwork; the repair of cracks, blisters, and flaws in iron and steel castings, forgings, &c.; as a substitute for brazing in many instances.

**Metal cutting by oxygen.** This process is based on the well-known fact that a jet of oxygen directed upon a previously heated spot of metal ignites it, with the result that the metal acting as its own fuel burns away rapidly in the form of metallic oxide.

In the year 1889, the late Mr. Thomas Fletcher, of Warrington, showed that, after heating an iron plate to incandescence by means of the oxygen and coal-gas flame obtained with one of his blow-pipes, it was possible, by largely increasing the supply of oxygen, to 'fuse' holes and even slots in the plate.

Twelve years later, the same process was applied practically by Dr. Menne, of Germany, to the opening up of tuyeres in blast furnaces which had become blocked by the solidification of metal.

The use of oxygen for this latter purpose proved so successful that its value in the cutting of metal was again suggested. Theoretically, once iron is ignited in oxygen, if a powerful jet of the gas is maintained in contact with the metal, it is possible to burn away the metal without the aid of any auxiliary source of heat. In practice, however, is formed at a comparatively low temperature and lacks fluidity. It was found difficult in practice to eliminate all the oxide which was

formed. Much of it adhered to the partially molten metal, thus preventing the intimate contact of metal and gas, with the result that combustion soon failed, and the cutting operation was arrested. The process was in consequence intermittent, the consumption of oxygen wasteful, and the cut wide, coarse, and irregular. In 1904, a cutting blowpipe, which is a very simple solution of this difficulty, was patented and subsequently introduced by the Société Anonyme L'Oxydrique Internationale of Belgium. It consists essentially of an oxy-hydrogen, oxy-coal-gas or oxy-acetylene blowpipe, with an additional passage through which an independent and separately controlled stream of oxygen is supplied at the discretion of the operator. This separate supply of oxygen may be discharged through the centre of the blowpipe, in which case the mixed gases employed for heating are conducted through an annulus surrounding it, or the supply may be brought in a passage immediately behind the heating flame.

This simple expedient renders the cutting operation independent of the heating flame. The separate jet of oxygen furnishes the quantity of additional heat necessary to render the oxide fluid, so that it can be blown away through the cut by the separate jet of oxygen.

The cutting operation is very simple, and can be mastered by any intelligent workman in a few hours. The edge or surface of the plate at the point to be cut is first heated by the mixed jet of oxygen and any suitable fuel gas. When this spot has been brought to a state of incandescence, a fine cutting jet of oxygen is discharged upon it. This immediately produces combustion of the metal, with the resulting formation of iron oxide. The jet of oxygen is made sufficiently strong to blow away this iron oxide in front of it, with the result that a clean narrow cut is effected through the metal at a speed of travel which is comparable with hot sawing. The metal on each side of the cut is neither melted nor injured in any way, as the action proceeds too rapidly for the heat to spread; in fact the edges present the sharp and purely metallic surface of a saw cut.

The process is made to follow any desired profile, by means of purpose guides and other mechanical contrivances are employed. Bevel cuts can be made and the process can be

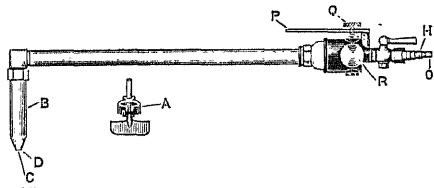


FIG. 7.

employed for the cutting of all grades or conditions of steel, as the action being chemical rather than mechanical the quality of the metal does not materially affect the results.

Fig. 7 illustrates a popular type of hand metal cutter, of the concentric type, in which

the oxygen for cutting is discharged through the centre of the blowpipe whilst the mixed gases for heating are conducted through an annular passage surrounding it, all gas supplies being separately controlled.

Special appliances are supplied for ensuring a steady movement of the hand cutter, a matter of considerable importance where neat and accurate work is desired. In fact, machines and appliances are constantly being devised with the object of extending the applications of the process and of improving the results obtained.

The process may be employed for cutting sections of any thickness up to and even exceeding 12 inches, and the same cutter can be employed without any structural alteration on plates varying in thickness within wide limits; all that is necessary is to increase the velocity and quantity of oxygen used for cutting, to correspond with the increased thickness of the plate.

As indicating the remarkable possibilities of this process, the following results obtained in the cutting of nickel-chrome steel armour plate are interesting.

With a single jet of oxygen, a plate  $9\frac{3}{4}$  in. thick was cut at the rate of one foot in  $3\frac{1}{2}$  minutes . . . . . of 30 cubic feet of oxygen per foot run.

A plate, 12 in. thick, was cut . . . . . rate of one foot in  $4\frac{1}{2}$  minutes . . . . . tion of 50 cubic feet of oxygen per foot run.

Such results as these indicate the immense field of operation both in constructional and destructional ironwork which lies before this important application of oxygen. K. S. M.

#### OXYHAEMOGLOBIN v. BLOOD.

**OXYLIQUIT.** Liquid air mixed with oxidisable substances, such as wood charcoal. Used as an explosive.

**OXYPHENINE** (*Chlorophenine, Chloramine Yellow, Diamine Fast Yellow B, 2 F, etc.*) v. PRIMULINE AND ITS DERIVATIVES.

**OXYPHLOROGLUCINOL v. PHENOL AND ITS HOMOLOGUES.**

**OZOKERITE**, known in Germany also as *Erdwachs, Bergtalg, Bergwachs Fossiles wachs, Mineralfett, mineralisches Leichenwachs*, in Moldavia also as *Zietrescit*, and in the neighbourhood of the Caspian Sea as *Naphtgil, Naphatil, Neftgil, Neftgil, Neftchil*, is a naturally occurring solid hydrocarbon of the olefine, or  $C_nH_{2n}$ , series. Ozokerite is found chiefly in the Miocene formation in Boryslaw, near Drohowycz, and in the region of Stanislawow, Galicia. The veins in which it occurs are 40 to 80 metres deep, and 1 metre in thickness. They pass through beds of sand, from 8 to 10 metres deep, containing large stones, and then through blue clay and a plastic loam. From this blue clay, naphtha usually springs. The centre of the basin is richest in wax; in some cases masses of such extent have been tapped that the miners have hardly had time to escape before the workings were filled with the plastic mineral. Such a deposit was found in the deepest shaft at Boryslaw, at a depth of 208 metres (227 yards). In general, however, the yield of wax varies at from 4 to 8 p.c. of the mineral extracted. Ozokerite was discovered in 1833 by Dr. Mayer, in Slanic in Roumania, and Glocker, who analysed

it in the same year, gave the mineral this name, deriving it from two Greek words meaning 'to smell' and 'wax.' It was discovered in Galicia by Doms in 1854. At first it was regarded as an unwelcome companion to the petroleum, as it frequently caused the timbering of the shafts to collapse. It was not until about 20 years later that this substance began to attain commercial importance, a method having then been discovered of producing from it a substance resembling beeswax and named *ceresin*.

In 1865, ozokerite, which had previously been regarded as a Crown mineral, was declared free, and the consequence was that a number of shafts were sunk in the district, and much speculation ensued. The land being parcelled out in small plots, the shafts were sunk in the immediate neighbourhood of each other, and much waste and danger ensued. In 1886, a law was passed, whereby the right of mining for ozokerite might be separated from the ownership of the land. In 1899, it was further enacted that shafts were to be at least 60 metres distant from one another. The extraction is now carried out under official supervision. In nearly every case the mineral is raised through vertical shafts or pits over which a wooden roof is erected. The section of the shafts in the first instance is 4 square metres (43 square feet); but, when the ozokerite formation is reached, an inner shaft 1 metre square (10.76 square feet) is formed of timber, and the space between this and the timbering of the larger shaft is filled with a rich clay. This construction is adopted to exclude the surface-water, which is now kept down by machine driven pumps during the sinking. From the bottom of the shafts levels are driven into the ozokerite ground, the richer portions being raised and the refuse used to fill up the old workings. The softer parts of the marl are dislodged by means of pick or wedge; but where the rock is hard, and the permission of the mining authorities can be obtained, dynamite is used. The mineral used to be raised by hand in skips or tubs holding 40 to 50 kilos. (88 to 110 lbs.). But electricity has now been applied to the haulage and this has greatly increased the output, two men now being able to raise 120 skips of 135 kilos. per day where four men were needed to raise 60 skips of 50 kilos. in the same time. Modern methods of ventilation and electric light have now mostly replaced the hand ventilators and safety lamps formerly employed. The timbering of the shafts is subject to constant renewal and repairs; in some cases it is almost impossible to keep the shafts perpendicular.

The water is usually raised in tubs, and much difficulty is experienced in getting rid of it after it reaches the surface, on account of the numerous shafts and the broken nature of the ground. Costly machinery for raising water by machines have now been introduced. The mineral, when it leaves the tubs, is sorted by hand. The waste rock is picked out and tipped to spoil, lumps of ozokerite are specially selected, and the remainder of the rock, containing fragments of wax, is tipped into tanks full of water. On being well stirred, most of the wax rises to the surface and is skimmed off. The residue still contains from 2 to 3 p.c.

of wax. A more costly, but more thorough, method of separating the wax is sometimes employed. The mineral, after being hand picked, is tipped into cast-iron vessels, and water at 50° is poured over it. The tanks are heated gradually from below, until the water boils. At 60°-70°, the melted wax which rises to the surface is ladled off and poured into cold water where it solidifies, after which it is removed and the water contained in its pores removed by pressure. A further quantity of wax is obtained by stirring the remaining hot contents of the tanks. This process is known as Lep-boiling (Lepkochen) (J. Soc. Chem. Ind. 1892, 117; *ibid.* 1898, 236; Eng. Pats. 2242, 1890; 9781, 1891; Die Zeresinindustrie, by Bela Lach, 1911). The quantity of waste mineral being considerable, and the distance between the shafts small, a special railway has been built to remove the residues from the immediate neighbourhood of the mines.

It has also been attempted to extract the wax by means of solvents such as benzene, but only with very poor results. The wax so obtained is of a much lighter colour and higher melting-point (73°) than the ordinary kinds, but is, nevertheless, not so useful in the ceresin industry.

The annual production has varied from 4000 to 18,000 tons, and in certain years the value has exceeded 1,800,000 dollars.

The production of ozokerite in the Boryslaw district amounted, in 1887, to 96 p.c. of the total output in Galicia, and was valued at £152,900 (J. Soc. Chem. Ind. 1887, 614, 651; J. Soc. Chem. Ind. 1890, 597; *ibid.* 1892, 117; *ibid.* 1897, 774).

Since the production of ozokerite has become more costly, its output has decreased. Thus in 1904, Galicia, which practically supplies the whole world with the crude product, only produced 2908 tons.

The ozokerite forms lumps and layers from 3 to 9 decimetres thick, so that masses are often found about 100 kilos. in weight.

Other deposits of ozokerite are found at Truskawice, Starunia, Dwiniacz, Klecany, and Pruthale, always in Miocene formations.

It has also been found in Hungary by the river Iza in the neighbourhood of Pecora. Its quality here is inferior to that in Galicia, but it has not been systematically worked up. In various parts of Roumania also, excellent ozokerite deposits exist which have not yet been exploited.

Ozokerite is found in the Caucasus, and among the Wasatch Mountains, Utah, about 173 miles east of Salt Lake City, America, where deposits of white ozokerite, miles in length, are said to be found.

Caucasian ozokerite resembles an inferior Galician variety. Melting-point of crude substance 68°. Treated with 20 p.c. of fuming sulphuric acid it yields 58.1 p.c. of second-quality ceresin; m.p. 68.5°; volatile portion, 1.8 p.c. The crude substance has a repulsive odour, is worked with difficulty in quantity, becomes stiff in the basin, and presses extremely badly (Lach, J. Soc. Chem. Ind. 1885, 488).

Rich deposits of ozokerite have also been found along the banks of the Kemioki near Tornea (J. Soc. Chem. Ind. 1901, 1043) and in

the Island of Chelekon in the Caspian Sea (*ibid.* 1896, 932).

*North American or Colorado ozokerite.* Here extensive deposits of an ozokerite-like substance are found, the supply from which is hindered only by the transport difficulty. On being tested, however, the material seems to be of little use for the production of ceresin. It is supplied in cakes 36 × 20 × 6 cm. in dimensions. It is a dull black, hard substance, brittle and pulverisable, and smelling of catechu. Care must be taken in heating it, as violent frothing may occur from the presence of water.

The crude substance melts at 76.0°.

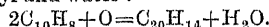
Treated by the above-mentioned process no ceresin is obtained. Even when heated to 300° it is impossible to filter it, although it is quite a thin fluid. Subjected to distillation it gives the following results:

	Per cent.
Paraffin oil . . . . .	90.00
Gas . . . . .	2.12
Water . . . . .	2.60
Residue . . . . .	5.28

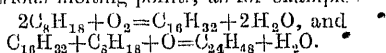
It commences to distil at 360°, when nearly 3 p.c. of oil, solidifying at 30°, comes over. At a much higher temperature it distils steadily, giving a very fair crude product for paraffin extraction. This substance is apparently more suitable for . . . . . than for the ceresin industry (B. . . . . Chem. Ind. 1889, 696).

In Utah, a dark brown ozokerite of m.p. 53°-55°, sp.gr. 0.9285, has been found (Seal, J. Franklin Inst. 1890, 100, 402; Parker, J. Soc. Chem. Ind. 1891, 736). Ozokerite is also found in Portuguese East Africa, in Ghazaland, and in many other parts of the earth, but generally either in too small quantities or of too poor a quality to make its extraction on a large scale profitable.

It varies largely in composition, in m.p. (56°-100°), in b.p. (210°-300°), and in sp.gr. (0.85°-0.97°), depending on its source. The native ozokerite is transparent, of a light-yellow colour, and of the hardness of beeswax. It smells like benzene or petroleum, but the harder varieties are almost odourless. The best ozokerite is yellow or greenish, and can be easily compressed between the fingers. This kind, however, is not much used for the preparation of ceresin. Ozokerite consists chiefly of heavy saturated hydrocarbons, together with unsaturated hydrocarbons and other substances (Gosling, J. Soc. Chem. Ind. 1898, 741; Israti, Chem. Zentr. 1897, i. 1222; *ibid.* 1904, ii. 1448; Fader, *ibid.* 1905, i. 1666; Morozewicz, *ibid.* 1909, i. 1113). It appears to have been formed by the oxidation and decomposition of the hydrocarbons of naphtha, since the action of oxygen on these compounds simply eliminates hydrogen. Thus, for example, naphthalene gives dinaphthyl and water:



By further oxidation compounds are obtained of the formula  $C_nH_{2n}$ , which react with the hydrocarbons of the marsh-gas series, with formation of very complex carbon compounds of various melting-points, as for example:—



According to this hypothesis, the formation of ceresin from naphtha by the oxidation of the compounds of the marsh-gas series, and the relationships of ozokerite, naphtha, and coal, can be explained in the simplest manner (Gosling, *l.c.*; Engler, *Chem. Zeit.* 1906, 30, 711; Künkler and Schwedhelm, *Chem. Zentr.* 1908, i. 1322; Rakusin, *J. Russ. Phys. Chem. Soc.* 1909, 41, 109).

The best kinds of ozokerite are used in the preparation of ceresin. For this purpose, the crude ozokerite is broken into small pieces and melted in tanks by the aid of steam coils. The mass is run into retorts and distilled with steam. When the distillate has cooled to an oily mass it is subjected to hydraulic pressure, after which it is again melted and treated with fuming sulphuric acid in vessels fitted with stirrers. A full description and figures of the plant and materials employed is given by Lach in his *Zeresinfabrikation*, 1911; *v. also* Gosling, *l.c.*). A number of methods of purification are also described in this work (*v. also* Marcusson and Schlüter, *Chem. Zeit.* 1907, 31, 348).

Good ceresin is not easily distinguishable from beeswax. The best methods of preparation are the best methods of distinguishing ceresin. Ceresin is not so easily kneaded between the fingers as beeswax, and is more brittle. A mixture of the two bodies cannot be recognised in this way. (2) Ceresin is almost unacted on by concentrated sulphuric acid, whilst beeswax undergoes perfect decomposition by such treatment. To reduce its cost and also to render it harder and more wax-like, ceresin is often adulterated with paraffin, rosin or colophonium, petroleum oil, or with carnauba and Japan wax.

In addition to the production of ceresin, ozokerite is used in the manufacture of candles, ointments, pomades, and shoe blackings. It is also employed to some extent in the manufacture of shining black paper and for the impregnation of certain kinds of wood in furniture manufacture.

Under the name of *okonite*, the residue remaining after the purification of ozokerite forms an excellent insulating material for electric cables (*J. Soc. Chem. Ind.* 1905, 518) and with an admixture of 50 p.c. India rubber, ozokerite is recommended as a very good insulating material.

Paraffin was formerly obtained from ozokerite by distilling the residue, forming ozokerite pitch.

*Ozokerite vaseline* is obtained by allowing melted ozokerite to pass through 12-30 filters of animal charcoal (depending on the degree of decolourisation required). The mass is then treated with superheated steam for 3-4 hours at 250° (*Gosling, l.c.*).

**OZONE**, or *active oxygen*. Sym.  $O_3$ ; molecular weight, 48. Van Marum, in 1785, noticed that air or oxygen in the vicinity of an electrical machine, or in the vicinity of electric sparks had been passed, acquired a peculiar odour, somewhat resembling that of chlorine; and Cruickshank, in 1801, noticed a similar smell during the electrolysis of water. But Schönbein, in 1840, was the first to recognise that this smell was due to the formation of a new gas, to which he gave the name ozone (*ὄζον*, to smell). Shortly afterwards he found

that ozone was also formed by the action of moist air on phosphorus. At first this substance was considered to be an oxide of hydrogen, but the researches of Marignac and De la Rive, of Andrews and Tait, of Fremy and Becquerel, of Brodie, and others, and especially of Sorét, established the fact that ozone is an allotropic form of oxygen produced by the condensation of three volumes of oxygen into two of ozone; or, in other words, that, whilst the molecule of oxygen contains two atoms, that of ozone contains three. Its formation may be expressed by the equation  $3O_2 = 2O_3$ . One view held for some time was that ordinary oxygen was composed of negative oxygen, or ozone, and positive oxygen, or antozone, the existence of the third form, or antozone, has been disproved.

**Preparation.**—As already stated, ozone is formed when a series of electric sparks is passed through oxygen or air, but the proportion of the oxygen so transformed is very small. A much larger proportion of ozone is formed when the silent discharge is substituted for the spark discharge, a contraction of the volume of air or oxygen occurring at the same time.

For this purpose a current of air or oxygen is passed between the terminals of an induction coil placed at a short distance apart and made as large in area as possible. The original Siemens 'induction tube' (1858) consisted of two concentric glass tubes, the outer tube being covered, the inner lined, with tinfoil. A current of air or oxygen is passed through the narrow annular space between the tubes, the metallic surfaces of the inner and outer tubes being connected with the terminals of an induction coil or electrical machine, and thus transformed into terminals of large area. A number of modifications of this apparatus have been employed. In some of these the metallic terminals are replaced by good conducting solutions, such as copper sulphate solution, &c., in others by shot, powdered graphite, &c., and the inner glass tube may be advantageously replaced by a metal tube. In many forms the terminals consist of flat metallic plates placed close together with a sheet of dielectric (glass, mica, &c.) between them, in others one or both poles consist of one or more points. Some inventors have claimed to get better results without the solid dielectric, relying only on the thin layer of air or oxygen between the plates as the dielectric. There is, however, little doubt that the solid dielectric between the electrodes is advantageous; on the one hand, acting as a condenser it increases the regularity of the discharge, and on the other, it very greatly reduces the tendency to sparking. But in all cases the principle is the same, viz. the passage of a current of air or oxygen between terminals of large area, placed very close together, and thus offering as little resistance as possible to the silent discharge and reducing sparking to a minimum.

More ozone is obtained when a current of oxygen is used than when air is employed. The proportion is also increased by thoroughly drying and cooling the oxygen, by increasing the pressure of the air or oxygen, and by bringing the terminals as near together as possible. Sparking is very detrimental, destroying much of the ozone formed. The best result is obtained when

there is a continuous 'glow' discharge. If the air is moist, some nitric acid is almost invariably formed. Under favourable conditions, and when great care is taken to keep the temperature of the apparatus and gas low, about 25 p.c. of the oxygen may be converted into ozone; but ordinarily, or on the large scale, the proportion obtained is much smaller.

Briner and Durand (Compt. rend. 1907, 145, 1272), by immersing their ozoniser in liquid air at a temperature of  $-194^{\circ}$  succeeded in converting 99 p.c. of the oxygen into ozone. In a bath of liquid carbonic anhydride and ether ( $-78^{\circ}$ ), only about 11 p.c. of the oxygen was converted. In the liquid air-bath the optimum pressure is about 100 mm., when the yield of ozone reaches about 55 grms. per kilo-watt-hour. As the pressure increases or decreases the yield decreases, being about 29 grms. at 255 mm., and 37 at 45 mm. Even at  $-194^{\circ}$  the spark discharge only gives about 1 p.c. of ozone, and the authors suggest that even this amount is probably due to the action of the silent discharge simultaneously occurring. The authors found that under the conditions of their experiments very little heat was produced by the silent discharge, the evaporation of the liquid air-bath being hardly appreciably greater when the electric current was passing than when it was not.

The yield of ozone produced by the action of the silent discharge varies greatly under varying conditions, which will be considered later under the section *Industrial preparation*.

Schmibtin noticed the formation of small quantities of ozone when phosphorus, partially covered with water, was left in contact with air. The phosphorus is oxidised to phosphoric acids, traces of

at the same time, together with some hydrogen peroxide. According to Van't Hoff (Zeitsch. physikal. Chem. 16, 411) 4 atoms of phosphorus can cause the production of 1 mol. ozone. If the ozone remains in contact with the phosphorus it is soon decomposed again, as it oxidises more of the phosphorus. The best results are obtained by passing a rapid current of air through a tube or bottle containing moist phosphorus at about  $24^{\circ}$ , but the quantity of ozone formed even then is very small. The action does not take place at ordinary atmospheric pressure below  $6^{\circ}$ , and the optimum temperature is about  $24^{\circ}$ . Under reduced pressure the action still takes place at  $0^{\circ}$ . The addition of sulphuric acid and permanganate or dichromate to the water increases the yield of ozone. Dry phosphorus does not readily cause this reaction, but it is found that if the surface of the phosphorus is occasionally fusing it, ozone is

produced in the presence of water. Pure oxygen does not readily give this reaction unless its pressure is reduced. A mixture of oxygen with three or four times its bulk of hydrogen gives rather more ozone than air does, but the reaction is dangerous, as the phosphorus may become heated to the ignition point of the mixture and cause explosion. The slow oxidation of turpentine, oil of cinnamon, and many other organic substances, is also accompanied by the formation of traces of ozone.

The action of concentrated sulphuric acid on the peroxides of barium, sodium, hydrogen, &c., and on the salts of the per-acids at low tempera-

tures yields oxygen containing small quantities of ozone. Potassium permanganate or dichromate give with strong sulphuric acid strongly ozonised oxygen.

If pure potassium chlorate is heated pure oxygen is produced, but if the ordinary commercial salt is used or manganese peroxide or another peroxide is added the oxygen evolved contains traces of ozone.

Crystallised periodic acid when heated at  $130^{\circ}$ – $135^{\circ}$  breaks up into water, iodic anhydride, and strongly ozonised oxygen (Rammelsberg), and aqueous solutions of the acid and of its sodium salt gradually acquire the smell of ozone.

Fluorine decomposes water and this reaction, even at low temperatures, is accompanied by the formation of appreciable quantities of ozone, amounting sometimes to 10–12 p.c. (Moissan). If water is dropped into a tube of fluorine, deep blue vapours of ozone are evolved.

Malaquin (J. Pharm. Chim. 1911, [vii.] 3, 329) has described a new and convenient method of preparing small quantities of ozone. 20 grms. of ammonium nitrate mixed with 15 grms. of nitric acid in a flask, the air displaced by carbon dioxide and the mixture then carefully heated to  $65^{\circ}$ – $75^{\circ}$ . The reaction, which is exothermic, then proceeds rapidly, and the resulting gas, after passing through weak potash solution,

contains ozone, mixed with about 90–92 p.c. oxygen and 4–5 p.c. nitrogen. It is not possible to use larger quantities of the mixture, nor to increase the quantity of nitric acid.

The oxygen evolved at the positive electrode during the electrolysis of strongly acidulated water contains ozone when the anode is composed of a non-oxidisable material, such as gold, platinum, lead peroxide. But under ordinary conditions the quantity formed is very small, especially if the surface of the electrode is large. The quantity of ozone produced is increased by increasing the intensity of the current, by decreasing the surface of the anode, and by reducing the temperature. Fischer and Massenez (Zeitsch. anorg. Chem. 1907, 52, 202) used as anode a narrow platinum tube coated with glass with a narrow slit cut through the glass so as to expose a very small surface of platinum. The anode was kept cool by passing through it a current of calcium chloride solution at  $-14^{\circ}$ , and the electrolyte itself (sulphuric acid with five times its volume of water, i.e. just below the concentration of maximum density) was kept at  $0^{\circ}$ .

The gas evolved contained 28 p.c. of ozone by weight. Fischer and Bendixsohn (Zeitsch. anorg. Chem. 1909, 61, 13, 153), by embedding platinum foil in glass and grinding away the edge so as to expose a line of platinum of 0.01 mm. width, have obtained oxygen containing 23 p.c. of ozone. Archibald and von (Elektrochem. 1911, 17, 812)

found that in the electrolysis of dilute sulphuric acid the yield of ozone may be considerably increased when an alternating current is passed in addition to the direct current used for electrolysis. The alternating current apparently depolarises the electrodes, in consequence of which more of the atomic oxygen liberated at the anode re-combines to form ozone



than under ordinary conditions. The authors found that of the anodic oxygen produced by the direct current, as much as 37 p.c. may be evolved in the form of ozone, although, owing to the large amount of gas produced by the alternating current, the content of ozone in the total anodic gas does not exceed 12 p.c. The electrolytic preparation is convenient for laboratory work, high concentrations being obtainable, but the consumption of current is large, and of all proportion to that of the silent discharge method—so that there is little likelihood of its being commercially available.

The formation of ozone being a strongly endothermic reaction, Nernst (Zeitsch. Elektrochem. 1903, 9, 891) argued, from theoretical considerations, that at high temperatures oxygen should become self-ozonised, and that at 6640° oxygen must contain 10 p.c. of its volume in the form of ozone. Much experimental work was carried out to try and produce ozone by heat alone, but without success. However, Fischer and Brachmer (Ber. 1906, 39, 940), Fischer and Marx (*ibid.* 1906, 39, 3631; 1907, 40, 443), and Fischer and Wolf (*ibid.* 1911, 44, 2956), have proved the correctness of Nernst's views. The decomposition velocity of ozone at 1000° is so enormous that at that temperature 1 p.c. would be reduced to 0.001 p.c. in 0.0007 seconds. The only chance of obtaining the ozone formed at the high temperatures is, therefore, by cooling instantaneously, i.e. more rapidly than the decomposition velocity. This was effected by carrying on the heating or combustion in contact with liquid air or liquid oxygen. Flames of hydrogen, and acetylene of 1 c.m. length burning at the nozzle of a narrow quartz tube were plunged into and continued burning in liquid air or oxygen. Flames of CO and  $\text{SH}_2$  could not be made to burn in the liquid oxygen, but were made to impinge on its surface. Burning sulphur and burning charcoal were thrown on to the surface of liquid oxygen. In all these cases ozone was obtained, the cooling effected by the liquid oxygen being more rapid than the rate of decomposition, the ozone formed was at once cooled and immediately dissolved in the liquid air or oxygen. When a glowing Nernst pencil at a temperature of about 2200° was plunged into liquid oxygen, ozone was produced, and when the experiment was continued for 10 hours nearly 4 p.c. of the oxygen was converted into ozone. Ozone was obtained when a current of oxygen or air was made to impinge on a glowing Nernst pencil in liquid air, or through a perforated pencil. With moist oxygen or with a fine stream of water hydrogen peroxide is also formed, and with air oxides of nitrogen are present. In the latter case, the slower the stream of air the more oxides of nitrogen are produced, the more rapid the stream the more ozone. With a stream of air of velocity above 30 metres per second ozone alone is produced, and below 5 metres per second only oxides of nitrogen. When an electrically heated platinum wire at 1700° was plunged in liquid air ozone was formed, but no nitric oxides. In liquid oxygen the platinum wire fused after disintegration, but by glazing it with zircon chloride or yttrium nitrate, the platinum wire lasted some minutes, and ozone was then produced. The arc light in liquid air produced

ozone and oxides of nitrogen. In these reactions with air currents short heating and rapid cooling produced mainly ozone, long heating and slow cooling mainly oxides of nitrogen, and long heating and rapid cooling mixtures of ozone and oxides of nitrogen.

In the combustion of hydrogen hydrogen peroxide was among the products. By varying the conditions the authors were able largely to control the formation of the various products. With the Nernst pencil in liquid air the action of the electric energy in the form of heat approximates to the same order of magnitude as it does in the silent discharge. A rapid stream of air or ozone was blown against a Bunsen flame produced by hydrogen, and has been suggested as a technical method; but though the actual energy consumed in using high temperatures alone may not be excessive, the other conditions render its technical application hopeless.

The cathode rays and the ultra-violet light rays acting on air or oxygen produce ozone, and this action is much increased at low temperatures. If liquid oxygen is exposed to these rays ozone may be detected on evaporating the oxygen. If solid oxygen snow is dipped in liquid hydrogen and exposed to the ultra-violet rays, the oxygen, after evaporation of the hydrogen, is found to contain ozone (Dewar). The action of the ultra-violet rays in the sun's rays, on the upper layers of the atmosphere, is almost certainly one of the main causes of the ozone present in the atmosphere. But whilst the ultra-violet rays produce ozone from oxygen, they also have a destructive action on ozone already formed.

The rays emanating from strongly radioactive metals and their salts produce traces of ozone when acting on air or oxygen (Curie, Compt. rend. 1899, 129, 823).

Ozone is produced in minute quantities during the evaporation of water, especially when the latter is in the form of spray, and this forms one source of the ozone present in sea air.

**Properties.**—In almost all its modes of production ozone is mixed with considerable, generally with very large quantities of oxygen or air. In this diluted state it has a strong and characteristic odour, somewhat resembling that of dilute chlorine, and appears colourless unless viewed through layers of several feet when its blue colour becomes visible. The odour is distinctly detected in the atmosphere as a part of ozone in the atmosphere (Chappuis and Chappuis (Compt. rend. 1882, 94, 1249) first succeeded in separating approximately pure ozone by carefully compressing ozonised oxygen to 125 atmospheres pressure at the temperature of liquid nitrogen (77°). The ozone condensed as a blue liquid, the supernatant being a highly compressed gas being colourless. Liquid ozone mixed with some liquid oxygen is obtained when a current of ozonised oxygen is passed into a tube placed in a bath of liquid oxygen. Ladenburg (Ber. 1898, 31, 2508 and 2830), by the careful fractionation of the mixture thus formed, obtained ozone of a purity of 84.4 p.c. When strongly ozonised oxygen is bubbled slowly through liquid oxygen

<sup>1</sup> During compression care must be taken to keep the temperature from rising much, as otherwise the ozone is liable to explode with great violence.

in a tube, a mist gradually forms above the surface of the oxygen, and after a little while a dark blue drop of liquid ozone forms just above the surface (Devlar). On raising the tube a little this drop may be brought into contact with the liquid oxygen in which it immediately dissolves. Liquid ozone is a very deep blue, almost black liquid which is transparent in thicknesses of less than 2 mm., but above that thickness is almost opaque. It was first given by Olszewski (1867, 8, 69) as  $-106^{\circ}$ . A careful re-determination by Troost (Compt. rend. 1898, 126, 1751) gave  $-119^{\circ}$ . Liquid ozone is fairly stable at temperatures below its boiling-point, and may be distilled if contact with organic matter or other oxidisable substances is avoided, but the least trace of such substances causes violent explosion. The gas is formed by the vapourisation of the liquid is dark blue in colour and is very unstable, exploding violently on a slight rise in temperature or by contact with a trace of organic matter or easily oxidisable substance. As is natural for a thermic compound the gas undergoes spontaneous decomposition. Experiments have been made as to the decomposition of ozone in admixture with air and oxygen, owing, in many cases, to the presence of traces of impurities in the samples tested, but the recent researches of Chapman and Jones (Chem. Soc. Trans. 1910, 97, 2463; 1911, 99, 1811) have cleared up the doubtful points. The decomposition, which is very slow at low temperatures, is greater the more ozone is present, increases rapidly with rise of temperature—at  $100^{\circ}$  from about one-half to three-quarters is destroyed in half an hour—and is almost instantaneous at  $300^{\circ}$ . The decomposition at high temperatures is accompanied by phosphorescence, which is very marked when a hot glass rod is brought near the decomposing gas. The phosphorescence when passing ozone vapour through a capillary opening. The presence of oxygen, nitrogen, carbon dioxide, and moisture have no influence on the rate of decomposition in the presence of traces of oxides of nitrogen, chlorine, phosphorus pentoxide, &c., very considerably accelerate it. Reduction of pressure also increases the rate of decomposition.

Ozone is decomposed in unlimited quantity by the peroxides of manganese, cobalt, nickel, and lead, by the oxides of copper and iron, and also by silver leaf, the oxides or silver undergoing no permanent change. These effects are probably due to the successive or simultaneous formation and decomposition of higher oxides. In the case of silver leaf the alternating formation and decomposition of silver oxide may be observed. In some cases ozone acts, like hydrogen peroxide, as a deoxidising agent on highly oxidised compounds. Thus hydrogen peroxide is reduced to water, and barium peroxide to the monoxide. In these cases the ozone is simultaneously decomposed:  $O_3 + H_2O_2 = 2O_2 + H_2O$ . Ozone is also decomposed when agitated with powdered glass, or by passage over spongy platinum or palladium. It is, however, without action on permanganic or perchromic acids.

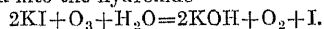
Very varying statements are made as to the

solubility of ozone in water, some observers stating that it is insoluble. It is undoubtedly somewhat soluble, although the degree has not yet been satisfactorily determined. Various causes are probably contributory to these discrepancies. The tests have generally been carried out with very dilute mixtures, and the experimental figures so obtained multiplied up to correspond to pure ozone. The experimental error is thus very largely increased and is further augmented by the partial decomposition of the ozone during the tests, the very great variation in solubility at varying temperatures and possible deviation from the law of solution according to partial pressures. From some of the most trustworthy results it appears to be at least ten times as soluble in water as oxygen is. Thus Carius found the coefficient at  $1^{\circ} = 0.834$ , Schöne at  $18^{\circ} = 0.366$ , and McLeod at  $14^{\circ} = 0.274$ . Mailfert (Compt. rend. 1894, 119, 951), working with an air containing 3.5 p.c. by volume of ozone, gives the solubility as 0.64 at  $0^{\circ}$ , 0.5 at  $11.8^{\circ}$ , 0.27 at  $27^{\circ}$ , 0.03 at  $55^{\circ}$ , and 0.0 at  $60^{\circ}$ . Ladenburg, on the other hand (Ber. 1898, 31, 2510), gives the solubility as 0.01 by volume. The solution acts as a powerful oxidiser, and has the characteristic odour of ozone. The ozone in solution gradually disappears, and simple agitation of ozonised oxygen with water destroys much of the ozone.

The so-called ozone water of commerce generally contains no ozone, its activity being due to hypochlorites, nitrous acid, &c.

Ozone is a very strong oxidising agent, giving up one-third (one atom) of its oxygen very readily. Thus it converts copper, mercury, silver, iron, and most other metals into the corresponding oxides, but this reaction appears to require the presence of traces of moisture. Only gold, platinum, and some other metals of the platinum group are unattacked. Ozone has a remarkable effect on mercury, one bubble of oxygen, containing  $\frac{1}{50}$  of its bulk of ozone, being sufficient to alter the physical condition of several pounds of mercury. The mercury loses its mobility, convexity of surface and lustre, and adheres to the surface of glass. If the ozone is moist, permanent oxidation takes place, but if perfectly dry the mercury is said to recover its usual physical properties when exposed to dry air. Ozone oxidises lead sulphide to sulphate, ferrocyanides to ferricyanides, manganous to manganic compounds.

Moist ozone oxidises phosphorus, sulphur, selenium, tellurium, and arsenic to phosphoric, sulphuric, selenic, telluric, and arsenic acids respectively, ammonia to nitrous and nitric acids, and silver and lead to their peroxides. Ammonia is oxidised to ammonium nitrite and nitrate, and hydrochloric, hydrobromic, and hydriodic acids are oxidised to water and the free halogen. Traces of ozone hinder the combination of hydrogen and chlorine, and traces of chlorine hinder the formation of ozone by the action of the silent electric discharge. It liberates iodine from potassium iodide, the potassium being converted into the hydroxide



This reaction forms one of the best means of estimating the amount of ozone in a gas, as the amount of iodine can readily be estimated by titration. But in large excess ozone, in presence

of the alkali, oxidises some of the iodine to form iodite, iodate, and even periodate (Garzaroli-Thumackh, *Monatsh.* 1901, 22, 455).

Ozone oxidises most organic compounds, destroying caoutchouc and vulcanite, for instance, so readily that these cannot be used for making connections in its preparation. It bleaches most vegetable colouring matters (indigo, litmus, &c.), and decolourises blood.

In most of the above oxidations the volume of the gas remains unaltered, the molecule of ozone giving up one atom of oxygen to the substance and forming a molecule of oxygen:  $\text{Cu} + \text{O}_3 = \text{CuO} + \text{O}_2$ . In the oxidation of oil of cinnamon, and many other oils, however, absorb the ozone molecule as a whole, and the reaction has been utilised to determine the composition of ozone. Thus, if a carefully measured quantity of dry oxygen is ozonised, the contraction carefully noted, and then the resultant gas shaken with turpentine, the ozone is absorbed with a further contraction, twice as great as the first, the remaining gas being oxygen. This points to the contraction of three volumes of oxygen to form two of ozone, and this result has been confirmed by Soret and others, who also determined the relative rates of diffusion of mixtures of ozone and oxygen and of chlorine and oxygen. The molecule of ozone, therefore, contains three atoms of oxygen, one of which is easily liberated in the nascent state, and forms a compound, viz.  $\text{O}_3 = \text{O}_2 + \text{O}$ . In certain cases, e.g. with iodine, however, the ozone molecule acts as a whole, no free oxygen being liberated. This, as originally noticed by Brodie, is particularly the case in its oxidation of gases, sulphur dioxide, for instance, being directly oxidised to sulphur trioxide  $3\text{SO}_2 + \text{O}_3 = 3\text{SO}_3$  (Riesenfeld, *Zeitsch. Elektrochem.* 1911, 17, 634).

Some unsaturated organic compounds containing double linkings absorb oxygen to form comparatively stable *ozonides* (see OZONIDES), but Molinari finds that compounds with treble linkings do not form these derivatives and proposes this reaction for distinguishing between double and treble linkings.

Hydrogen is not oxidised by ozone at ordinary temperatures, but is at  $100^\circ$ . Water is not directly converted into hydrogen peroxide. Carbon absorbs and decomposes ozone, but is not itself oxidised at ordinary temperatures.

Ozone acts on solid or strong solutions of potash at low temperatures to form an unstable brown compound, which is probably  $\text{K}_2\text{O}_4$  (Bayer and Villiger, *Ber.* 1902, 35, 3038); this may be looked upon as a salt of an *ozonic acid*  $\text{H}_2\text{O}_4 (\text{O}_3 + \text{H}_2\text{O} = \text{H}_2\text{O}_4)$ . On rise of temperature, or acidifying, oxygen and traces of hydrogen peroxide are formed, but no ozone. With lime water ozone produces a granular precipitate which is probably a peroxide. With acetylene ozone reacts with explosive force.

If gold or platinum plates are immersed in ozonised air or oxygen they are found to have become electro-negative to other similar plates. Copper is not affected by the action, but to a very much less degree.

The great chemical activity of ozone and its unstable character are largely due to the fact that it is a highly endothermic substance, and thus gives out a great deal of heat on decomposition. The following are the most important

determinations by various investigators of the heat absorbed in the formation of ozone from oxygen:—

Hollman, 1868	17,064 Cals.
Berthelot, indirect, 1876	29,800 "
Mulder and v. d. Meulen, indirect, 1882	33,700 "
v. d. Meulen, indirect, 1882	32,800 "
v. d. Meulen, direct, 1883	30,500 "
Jahn, direct, 1908	34,100 "
Kailan and Jahn, 1910 ( <i>Zeitsch. anorg. Chem.</i> 68, 243)	34,500 "
Kailan and Jahn, 1910 ( <i>ibid.</i> ), decomposition by hot pt. wire	34,000 "

Ozone gives an absorption spectrum consisting of numerous lines, of which the two most characteristic (of wave length 609.5–595.5 and 577–560) lie close on each side of the D line. Chappuis (*Compt. rend.* 1882, 94, 858) mapped 11 bands lying between the wave length 628.5 and 444. Schöne (*Zeitsch. anorg. Chem.* 1894, 6, 333) observed 13 more or less intense lines. Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.* 1900, 4, 125) noticed, in the spectrum of liquid ozone, a line in the red which only appears when about  $\frac{1}{2}$  of the ozone is considered as dissociated into molecular oxygen being present,

indications of which are to be found in other characteristics of ozone. Hartley (*Chem. Soc. Trans.* 1881, 39, 60, and 111) found many of the dark lines of the solar spectrum to be due to absorption by ozone present in the atmosphere and considered the colour of the sky to be largely due to this ozone. Meyer (*Ann. Physik.* 1903, [iv.] 12, 849) confirms Hartley's results and conclusions.

Ozone is more magnetic than oxygen, the ratio of its specific magnetism to that of oxygen being greater than the ratio of their densities.

**Oxozone.** Various workers have suspected the presence in ozone of a still more condensed form of oxygen. As already mentioned Ladenburg came to this conclusion from his study of the spectrum of liquid ozone, and in conjunction with Goldstein obtained ozonides containing the group  $\text{O}_4$ . Harries (*Zeitsch. Elektrochem.* 1911, 17, 629), by evaporating a mixture of liquid oxygen and ozone through a series of flasks, found the sp. gr. of the gas in the first flask was less than that of the gas in the second, and in the first flask liberated more iodine from potassium iodide than corresponded to its sp. gr., whilst that in the second liberated the expected amount. He then found (*Zeitsch. Elektrochem.* 1912, 18, 129) that whilst, as has been generally stated, moderately ozonised oxygen may be passed through caustic potash solution and sulphuric acid without appreciable loss of ozone, this is not the case with very concentrated ozonised oxygen, at all events when the latter has been produced by the silent discharge with a high tension current. Working with a mixture containing 11–14 p.c. of ozone produced by an 8000-volt current of 10 per second periodicity, Harries found that 3–4 p.c. loss of ozone occurred when the mixture was bubbled through a solution of caustic potash and a further 2–3 p.c. if it was subsequently passed through sulphuric acid. He has further (*Ber.* 1912, 45, 936), in conjunction

with some of his students, published the results of the action of the washed and unwashed ozone in the preparation of ozonides. He finds that butylene with the washed ozone produces the monomeric ozonide  $C_4H_8O_3$  and the dimeric ozonide  $(C_4H_8O_3)_2$ , but that with the unwashed gas the mono- and dimeric oxozonides  $C_4H_8O_4$  and  $(C_4H_8O_4)_2$  are also produced (Evers). Treating tetrahydrobenzene in hexane with the washed ozone the solid ozonide  $C_6H_{10}O_3$  is readily obtained, even without recrystallisation, whilst with the unwashed a mixture of the ozonide and the oxozonide is produced (Seitz). Caoutchouc similarly yields  $C_{10}H_{16}O_6$  and  $C_{10}H_{16}O_8$  (Hagedor). From these results there is no doubt of the presence of a compound  $O_4$  in ozone, and under the conditions in which Harries worked, he considers that of the so-called ozone about one-third was really oxozone. It is probable that the greater liberation of iodine just referred to is due to oxozone acting in a different manner from ozone on potassium iodide.

*Detection and determination.* Ozone is most readily detected by means of paper moistened with a mixture of starch and potassium iodide. If ozone is present, iodine is liberated, and the starch paper coloured blue. This reaction, however, is also produced by nitrous and nitric acids, by chlorine, &c., so that it is not conclusive. A more conclusive test is to take a piece of neutral litmus paper and moisten half of it with a neutral solution of potassium iodide. If now this paper is subjected to the action of ozone the potassium iodide is oxidised and caustic potash formed, which at once turns the litmus paper blue. The turning blue of the part of the litmus paper not treated with the iodide would indicate the presence of any ammonia, which might otherwise be taken for ozone. Chlorine, nitrous acid, &c., if present, would form a neutral potassium salt, or would show an acid reaction. If, then, the untreated end remains the neutral purple whilst the iodised end turns blue, the presence of ozone is fairly conclusively proved. The litmus may be replaced by phenolphthalein or by a solution moistened with guaiacum or with tetramethylene-*p*-phenyldiamine, both of which are turned blue by ozone, are very sensitive, but, like iodised starch paper, are also similarly acted on by other oxidising agents. Arnold and Mentzel (Ber. 1902, 35, 1324 and 2902) recommend paper soaked in solution of benzidine or of tetramethyl-di-*p*-aminophenylmethane. The benzidine is coloured brown by ozone, blue by nitrous acid, blue and then red by chlorine, and gives no reaction with hydrogen peroxide, hydrocyanic acid, sulphuretted hydrogen or ammonia. The 'tetramethyl base' gives violet with nitrous acid, and with nitrous fumes, deep blue with  $H_2O_2$  and no reaction with hydrogen peroxide. The sensitiveness of the reaction is increased by adding a trace of acetic acid. For the determination of ozone the reaction is satisfactory. It is best to pass the ozone through the neutral potassium iodide solution and acidify before titrating, but some investigators prefer to acidify before passing the ozone. In either case it is essential that a large excess of the iodide solution should be present, as other-

wise some oxidation of the liberated iodine may occur. Ladenburg (Ber. 1903, 36, 115) obtained satisfactory results by passing the gas through standardised potassium iodide solution and then titrating. If agents other than ozone are present, determinations should be made, the one of the gas in question, the second after the gas has been passed through a tube, heated at  $260^\circ$  to destroy the ozone. The difference of the two tests gives the ozone present. The presence of oxides of nitrogen may also be detected by passing the mixed gases into liquid air. The ozone is dissolved whilst even traces of nitrogen are at once solidified and removed.

The determination of the density of the ozonised air or oxygen has been used for measuring the amount of ozone present. Otto has designed a baroscopic apparatus for this purpose, and also a dilatometer for utilising for the same purpose the dilatation caused by decomposing the ozone at the temperature of boiling amyl benzoate ( $261^\circ$ ).

Ozone is present in minute quantities in the atmosphere. The maximum amount is certainly never more than 1 part in 450,000 of air. Its presence is probably the silent discharge of lightning, and accompanying the flash discharge of lightning, the evaporation of water, and especially of saline waters, as in the sea foam, the action of some vegetable products on the air, and, perhaps, in the greatest degree the action of the ultra-violet solar rays on the atmosphere. Wurster found (Ber. 19, 3208) that ozone is also formed by the action of sunlight on clouds. When clouds are continually formed from above (i.e. in sunlight), all become laden with ozone, whilst when they are formed from below the upper layers are much more charged than the lower.

The ozone present in the atmosphere probably plays an important part in keeping the air pure and fresh by destroying the deleterious organic matter constantly passing into the atmosphere from decomposing flesh, animal excreta, &c. In the open country, and especially by the seaside, ozone can always be detected, but in the air of large towns it is either absent or present in much smaller quantities. Richardson proposed (Aesclepiad, 1887) the artificial production of ozone for the purpose of purifying the air of sick-rooms and even of towns, but it is only recently that this use has been practically introduced.

When present in the air in very minute quantities ozone is very advantageous to health, but if the quantity present is enough to cause a strong odour it is found to have a very irritating and harmful effect on the mucous membrane and the system, causing headache, influenza, &c. If the quantity is large it becomes a strong irritant poison, causing acute inflammation, and leading to fatal results. Slightly ozonised air and oxygen is now sometimes used medicinally, especially in pulmonary complaints. Labbé has shown that ozone to the extent of 1 part in 20,000 may be inhaled for half an hour at a time without any ill-effects.

*Industrial preparation and applications.* In recent years the industrial preparation of ozone has been very greatly improved, and has developed into an important industry, which is

still growing rapidly. Of all the methods of producing ozone, the only one which seems technically economical is that by the action of the silent discharge in air or oxygen. Starting from the original Siemens ozoniser innumerable modifications have been proposed, but these may be broadly divided into three classes, and only a few of the principal can be referred to here. The first class comprises those with smooth electrodes of large area either in the form of concentric cylinders or parallel plates. The second comprises those having one or both of the electrodes more or less pointed; and the third is a combination of the first and second classes, wherein the plate electrodes are so modified or roughened as to virtually transform them into a very large collection of points. The majority of the industrial ozonisers have either one or two sheets of a solid dielectric between the two electrodes, through which some air or oxygen is alone passed as dielectric.

As already stated, the yield of ozone varies enormously under varying conditions of character of discharge, form of electrode, quantity and potential of current, &c. These conditions, which are very complicated, have been studied by numerous investigators, especially by Warburg and Leithauser, who have published very exhaustive and important results of their experiments (Warburg, *Ann. Physik*, 1901, 5, 781; 1902, 9, 1286; 1904, 13, 470 and 1080; 1905, 17, 6 and 20; *Proc. Roy. Soc. London*, 1904, 209; Warburg, *Ann. Physik*, 1906, 20, 73; *Ann. Physik*, 1906, 20, 73; *Ann. Physik*, 1906, 12, 409; Gray, *Sitz-Ber. K. Akad. Wissen. Berlin*, 1903, 1016; Harries, *Annalen*, 1906, 343, 334; *Ber.* 1906, 39, 3667; Askernasy, *Technische Elektrochemie*, 1910; H. de la Coux, *L'Ozone et ses Applications industrielles*, deuxième édition, Paris, 1910; de Kay Thompson, *Applied Elektrochemie*, Macmillan, 1911). Reference to these researches must be made for details, only some of the general results can be summarised. If a point distant 1 cm. from a plate connected to earth is charged negatively to 7000 volts in air, a bluish light surrounds the point. On raising the potential a red brush appears separated from the blue by a dark space, the plate remaining dark. From a positively charged point a reddish light appears at a low potential and a brush develops as the potential is raised. Old points tend to lose the power of forming the brush discharge, giving a spark instead, but the brush reappears if a small gap even of only 0.1 mm. is introduced before the points. If a point is connected to earth by a wire, a spark passes between a point and an earth-plate the positive brush is apparent, although by means of a revolving mirror it may be seen that the negative is actually alternately present. Between plates with solid dielectrics between them a uniform luminosity occurs with a high potential, a lower one tending to form brush discharges. As a general rule, other conditions being equal, the yield of ozone in proportion to the energy consumed is highest, (1) when the uniform luminosity can be maintained, and (2) the lower the temperature. The highest concentration of ozone is obtained with negative points, the highest yield with positive points. For concentrations up to 4 grms. per cubic metre positive points and

a high current are most economical, between 4 and 9 grms. per metre negative points and low currents (Warburg and Leithauser).

The production of ozone from oxygen by the silent discharge is accompanied by a simultaneous destruction of the formed ozone to oxygen, the rate of destruction increasing the greater the quantity of ozone and the higher the temperature. This, on the one hand, causes a limitation of the concentration obtainable, and on the other, a decreasing efficiency the higher the concentration. The technical standard of concentration is generally taken as grams of ozone per cubic metre of air or oxygen. The maximum concentrations obtainable technically are about 50 grms. with air and 150 with oxygen. These concentrations and yields, under the best conditions, with oxygen are about three times what they are with air—but for technical economy much lower concentrations are used. The concentrations at present employed are generally from 1 to 4 grms. per metre, the lowest concentration being selected which is consistent with the satisfactory carrying out of the process in hand. The cost per unit of actual ozone produced (i.e. consumption of energy per unit weight of ozone) increases rapidly with increase of concentration—an increase of concentration from 2 to 12 grms. means a loss of efficiency of at least 25 p.c. This must be borne in mind in comparing costs of ozone given in published statements, as in some cases where very low costs are claimed, the figures are based on such very low concentrations that the ozonised air or oxygen so produced is of very little technical value.

*Siemens and Halske ozoniser.* This consists of an inner cylinder of aluminium and an outer one of glass. Six or eight of these are enclosed in an iron case which is filled with water, the water acting both as cooling water and as the one pole, the iron case being earthed and so charging the water. The aluminium cylinders are connected with one pole of the high-tension apparatus. The current used is 8000–10,000 volts, and about  $\frac{1}{2}$  kilowatt is required for this unit.

*Andreoli ozoniser.* In this, which was one of the early practical forms of ozoniser, the plates consist of serrated bands of aluminium placed side by side with the points (17,700 in each unit) of each electrode facing one another and having a glass plate between the two plates.

*Otto ozoniser.* This consists of an iron cylinder through which runs an isolated rotating metallic axle on which are mounted a number of thin aluminium discs. The cylinder is connected with the one pole, the rotating axle with the other, and the discharge passes between the cylinder and the aluminium discs. No solid dielectric or cooling is used and the voltage employed is 80,000.

*Tindal-de-Prize ozoniser.* An iron half cylinder forms the one pole, and aluminium discs placed at right angles to the cylinder form the other. No solid dielectric is used and a voltage of 15,000–20,000 is employed. The whole is enclosed in a case, glass cylinders filled with glycerol being placed between the discs to prevent short circuiting or side discharges.

*Abraham-Marmier ozoniser.* In this apparatus large plates a metre square are placed in pairs

with a metal case filling the space between each pair. A stream of water for cooling runs through each metal case, and these cases are alternately connected to the two high-tension poles. A current of 15,000–20,000 volts is employed.

*Ozonair ozoniser.* This apparatus, which is now used extensively in England and on the Continent, consists of two plates made of an aluminium alloy gauze separated by a dielectric plate of micanite. It is claimed for this apparatus that the raised parts of the meshes act as rounded points in facilitating the regular flow of the current and so avoiding sparking, and that the open character of the plates cause the air circulation to prevent undue heating and obviate the need for water cooling. Several of these pairs of plates are enclosed in a case to form a unit. The voltage used is 5000–8000.

*Elworthy ozoniser.* The electrodes consist of metallic spirals surrounded by glass tubes, and the inventor claims that the spiral arrangement of the electrodes increases the yield of ozone. He employs a voltage of 11,000–12,000.

*Howard Bridge ozoniser.* In this apparatus the plate electrodes are perforated with conical holes, the air or oxygen passing in through these holes. The inventor claims that in this way the air passes more completely into the zone of electrical action than when it is introduced at right angles to the direction of the current, as is usually the case.

*Vosmaer ozoniser.* This consists of a series of parallel tubes each of which contains at opposite sides of the inner surfaces of the tubes two electrodes formed of strips of metal supported on porcelain insulators so that their inner edges, serrated in the form of a saw, point inwards towards each other.

*Gerard ozoniser.* In this the electrodes consist of concentric : with dielectric cylinders of glass or mica between them. The dielectric cylinder is supported at one place only, and the electrodes are cut or split so as to allow for free expansion. The ozonisers are collected in groups of ten, and the inventor claims that very high potential currents can be used without sparking, : in energy consumption the : claims to obtain 100 grms. ozone per kilowatt-hour and to reach a concentration of 30 grms. per cubic metre (Bull. Soc. Belge de l'Electric. 1910, 449).

In the technical apparatus described the air may be drawn or forced through as is most convenient. When dry air is used and the temperature kept down, about 40–60 grms. of ozone per kilowatt-hour is obtained at a concentration of about 2 grms. per cubic metre. If oxygen is substituted for the air, about 120–180 grms. of ozone is obtained. At lower concentrations with a rapid air current somewhat higher yields are obtained, at higher concentrations with a slower current lower yields. From thermochemical considerations the theoretical yield of ozone should be about 1.2 kilos of ozone per kilowatt-hour, so that the actual yield at present is with air only about 5 p.c. and with oxygen 15 p.c. of the theoretical. It is very probable that higher efficiencies may be obtained by improved ozonisers.

Erlwein (Zeitschrift für Sauerstoff und Stick-

stoff, 1911, 3, 143, 164, and 181) calculates from these figures that, including : interest on plant, depreciation

the cost of ozone, as it can now be actually technically produced from air, would be from 14d. to 22d. per kilo, from oxygen from 8d. to 11d. per kilo, to which latter figure has to be added the cost of the oxygen. This would compare very favourably with the cost of available oxygen from the oxidising agents usually employed.

At present by far the largest and most important application of ozone is in the purification : The Méritens in 1886 showed with bacteria were efficiently agitated with ozone the whole of the bacteria could be destroyed. Experiments to apply this fact to the industrial sterilisation of water were carried out in 1891 by Fröhlich and Werner Siemens, and an experimental plant was soon afterwards erected at Martinikenfeld. The first installation on a large scale was erected in 1893 by Schneller, van der Sleen and Tindal, at Oudshorn, Holland, for treating water from the Rhine, which contained from 5000 to 1,000,000 bacteria per c.c. This was followed by an experimental plant at the Hygiene Exhibition in Paris in 1895, and by an installation at St. Maur, near Paris, to sterilise two million gallons of water from the Marne per diem, both being erected by Tindal. About the same time Siemens and Halske put up large installations at Paderborn and Wiesbaden. Extended tests

conclusively proved that even on the industrial scale complete sterilisation of water can be effected by ozone. The pathogenic organisms are readily destroyed, the most resistant bacteria, as in most other antiseptic treatments, being the *bacillus subtilis*, the presence of which is harmless. Even when the water was intentionally very strongly infected with septic bacteria—in some cases to the extent of more than a million per c.c.—purification was complete. It is essential that the ozone be brought into contact with every particle of water to be purified, and for this purpose various forms of sterilising vessels have been used. The forms first used by Siemens and Halske and by Abraham-Marmier, consisted of wash towers filled with stones down which water in a fine state of division flowed, meeting an upward current of ozonised air. Otto used an 'emulsifier,' based on the principle of the Korting injector, to obtain his mixture of ozone and water, and in the Tindal-de Frize system the ozonised air was forced into water, flowing down towers containing horizontal perforated baffle plates. In more recent plant various modifications and combinations of these methods have been employed. In the Ozonair plant an additional chamber is employed where the water is, by means of special nozzles, atomised in an atmosphere of ozonised air. The amount of actual ozone needed to insure certain sterilisation varies according to the character of the water, but averages about 2 grms. per cubic metre (220 gals.), i.e. in the concentration of 2 grms. per metre of air usually employed, a bulk of ozonised air equal to that of the water to be purified. It is essential that the water should be free from suspended matter, and

if it is not it must be filtered previous to ozonisation. If the water contains dissolved organic matter this has a tendency to hinder sterilisation, and a larger proportion of ozonised air may be necessary. In the same way dissolved iron, which is oxidised and precipitated by the ozone, increases the quantity of the latter required.

Fresh installations have followed rapidly, and at the present time more than forty towns in Europe and America have adopted ozone purification of their water supplies. Amongst these are St. Petersburg (Siemens and Halske, 11,000,000 gals. per day), Nice (Otto 10,000,000 gals.), Florence (1,000,000 gals.), Philadelphia (Vosmaer, 1,000,000 gals. of water from the Schuylkill River, which is said sometimes to contain two and a half million bacteria per c.c., a large proportion of which are septic), and Lindsay, Ontario (Howard-Bridge, 1,500,000 gals.). At St. Maur two new installations are being erected, each to have a daily output of 10,000,000 gals., one having the Siemens-de Frise plant, the other the Otto-Abraham-Marmier. Hitherto there has been no similar plant in England, but the Ozonair Company have just completed an installation to treat the water supply of Knutsford, Cheshire.

The cost of sterilisation of water by ozone must vary with the quantity, the nature of the plant, &c. It should not exceed one penny per 1000 gals. of water, and for large installations may be less than a half-penny. The cost of each new installation at St. Maur for 10,000,000 gals. per day is to be £14,500, and from present working the engineer estimates that the cost of purification will be one-third of a penny per 1000 gals.

Portable ozone water purifiers were used with success in the early part of the war, small plants for domestic supplies are now manufactured, and there is a small automatic plant obtainable which can be attached to the water supply tap. This consists of a modified Körting injector attached to the tap and connected with a small ozonising plant. The current is taken from the house supply, and the act of turning on or off the tap automatically starts and stops the process.

Another important application of ozone which has made great progress is for the purification of the air in crowded and enclosed spaces. It is now recognised that the bad effects of the close air of crowded rooms, &c., is not due to the excess of carbonic acid or of moisture present, but to the traces of various organic exhalations coming from the lungs and skins of the people and animals present. These traces of organic matter are readily oxidised by ozone, even when the latter is present in such minute proportions as to be harmless and even beneficial when breathed. It has been found that the introduction of small quantities of ozone into close air has the result of removing the 'stiffness' and unpleasant effects, and making the air pleasant and healthy. It has been said that it also destroys the present, but for any real bactericidal effect a concentration of at least 1 part by volume of ozone in 2000 parts of air is necessary, a proportion which could not be breathed. The fresh air from outside coming in through the

ozoniser may very possibly be oxidised, and with the wall ozonisers of the air is caused, a part circulates through the ozoniser and may probably be oxidised. Large numbers of installations have been put into private houses, hospitals, theatres, and other public buildings, &c., and the process has just been adopted on a large scale for the purification of the air of the Central London Tube Railway. It has also been adopted with advantage in cold-stores, slaughter-houses, and factories or workshops where unpleasant smelling work is being carried on, for deodorising the air in Paris in connection with the washing of clothing.

As ozone can now be obtained at a moderate cost, has such active oxidising properties, and in oxidising introduces no foreign matter, it should find large application in the chemical industries. It has already been largely used in the production of vanillin by the oxidation of isoeugenol, one company making about 200 tons of vanillin per year in this way, and largely through this the cost has fallen from about £20 to £2 per lb.

Ozone is beginning to find applications for bleaching various substances, oils, fats, waxes, sugars, fabrics, &c. It is being used in the ageing of spirits and in leather curing.

Ozone is now being largely used in breweries with good results (Vetter, Woch. Brau. 1911, 28, 13, and 26; Vetter and Moufang, *ibid.* 1911, 28, 377). Passed through yeast the latter is greatly improved and strengthened, and the introduction of ozone into the air of fermenting rooms, &c., is being tried (Vetter and Moufang, *ibid.* 1911, 28, 13, and 26).

Ozone is also being used for the successful use for sterilising casks, pipes, &c., but this is controverted by Will and Beyersdorf (Zeitsch. ges. Brauw. 1912, 35, 73, and 89).

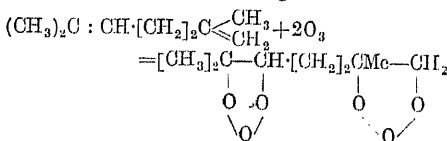
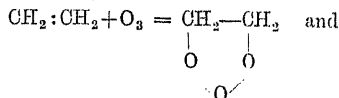
Ozone has been recommended and used for the bleaching of flour, &c., but it is not satisfactory for this purpose, acting detrimentally on the flour itself.

As already mentioned, ozone is now being considerably employed for medical purposes.

L. T. T.

**OZONIDES.** The term ozonide was originally applied by Schoenbein to certain metallic ozonides which, when decomposed, yield ozone. It has since been applied to certain organic ozonides (Chem. Zentr. 1897, ii. 45). The term is now used almost exclusively to designate the ozone derivatives obtained by the action of ozone on various classes of unsaturated organic compounds.

The reaction between ozone and an unsaturated ethylenic hydrocarbon may be represented by the equation



one molecule of ozone being added on for each ethylene linking. When heated or treated with





containing two double bonds are very readily decomposed. The 6- and 7-ring compounds seem to have similar stabilities towards boiling water, but the 5-ring compounds are much less stable than the two former classes. The ozonides of substances containing oxygen are very readily decomposed.

A large number of ozonides have been prepared of which the following may be described:

**Ethylene ozonide**  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O}_3 \end{array}$  is obtained by

treating an absolutely dry solution of ethylene in methyl chloride with dry 7 p.c. ozone at about  $-70^\circ$ , until the solution commences to be coloured blue. It forms a transparent colourless oil, b.p.  $18^\circ/16$  mm., with a pungent odour, is readily volatile and explosive. If the ozone used is of higher concentration or the reaction is continued beyond the production of the blue colour, an *oxozonide*  $\text{C}_2\text{H}_2\text{O}_4$  is formed (Harries and Koetschau, Ber. 1909, 42, 3305).

The ozonides and oxozonides of the homologues of ethylene are generally explosive, unstable substances, and have been obtained similarly, using ethyl chloride as solvent.

Ethyl alcohol, when treated with a stream of concentrated ozone, yields a peroxide, which has some of the properties but is not identical with ethyl hydroperoxide  $\text{C}_2\text{H}_5\text{O}\cdot\text{OH}$ .

... when treated with ozone, yield a type  $\text{RHC}:\text{O}:\text{O}$ , which have not been obtained pure, owing to the readiness with which they are transformed into the isomeric acid.

**Diallyl diozonide**  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_2 \cdot \text{CH} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{O}_3 \quad \text{O}_3 \end{array}$

formed by passing ozone into a chloroform solution of diallyl, is a colourless syrup which, when heated, yields succinic dialdehyde and a little succinic acid.

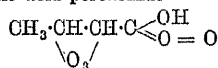
**Allyl alcohol ozonide**  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{O}_3 \end{array}$  is a

transparent syrup which decomposes at ordinary temperature.

**Allylacetone perozonide**  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)=\text{O} \\ \diagdown \quad \diagup \\ \text{O}_3 \end{array}$

is a clear explosive syrup which decomposes on treatment with water forming formaldehyde, laevulinic aldehyde and hydrogen peroxide.

**isocrotonic acid perozonide**

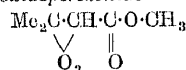


is a yellowish clear explosive syrup, which on standing, evolves oxygen and yields isocrotonic acid, whilst with water it yields acetaldehyde, glyoxylic acid and hydrogen peroxide.

**Mesityloxideozonide**  $\begin{array}{c} \text{Me}_2\text{C} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{O}_3 \end{array}$  is ob-

tained by treating 10 grms. well-cooled freshly distilled mesityl oxide with 12–14 p.c. ozone and a current of well-cooled carbon dioxide for about five hours, when a sample no longer decolourises an acetic acid solution of bromine. It is a thinner and less explosive oil than the perozonide, is miscible with all solvents except light petroleum and is readily decomposed by water and on heating.

When the mesityl oxide is saturated with ozone, *mesityloxideperozonide*



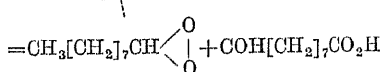
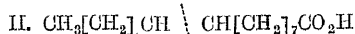
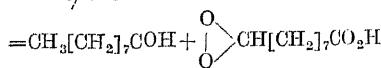
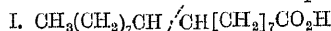
is formed as a thick green oil, highly explosive and spontaneously inflammable.

**Methylheptenone** yields similar normal and perozonides.

**Phorone** yields a monozone and a diozone—the latter being formed only very slowly when the treatment with strong ozone is very prolonged.

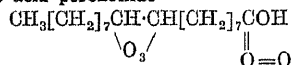
#### OLEIC ACID OZONIDES.

The *normal monozone*  $\text{C}_{19}\text{H}_{34}\text{O}_5$  is formed when oleic acid in acetic acid solution is treated with 0.5–18 p.c. ozone until a sample no longer decolourises a bromine solution of glacial acetic acid; or by washing the perozonide with water and sodium bicarbonate. It is a colourless, transparent, viscous liquid, heavier than water and when warmed with aqueous caustic soda yields a pleasant sharp smelling product, b.p.  $90^\circ$ . When treated with water it yields nonaldehyde, pelargonic acid, azelaic acid and an aldehyde product which, on oxidation, yields azelaic acid. The reaction is explained thus:



thus the primary products are nonaldehyde, nonaldehyde peroxide, azelaic acid half aldehyde (which is a decomposition product of almost all the ozonides of the higher aliphatic unsaturated acids), and the peroxide of the latter. By the isomerisation of the peroxides, pelargonic and azelaic acids are then formed. When warmed with glacial acetic acid the same products are obtained, but more peroxides are formed, whilst if formic acid is added to the acetic acid, considerably more aldehydes result. Similar products are also obtained by reducing the ozonide with sulphur dioxide or with aluminium amalgam in aqueous solution. Unstable ammonium, copper and sodium salts of oleic ozonide have been obtained.

**Oleic acid perozonide**



is formed when a glacial acetic acid or carbon tetrachloride solution of oleic acid is treated with 10–12 p.c. ozone for an hour for each gram of acid. It is a somewhat thicker liquid than the ozonide but has similar chemical properties to the normal ozonide. When oleic acid is treated with 10 p.c. ozone for a very long time (3 hours per gram) or for a somewhat shorter time (4 hours for 5 grms.) with 16–18 p.c. ozone,

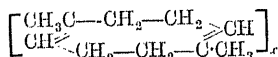
it yields a *superperozonide*  $C_{18}H_{34}O_7$ , possibly  $CH_3[CH_2]_7CH \cdot CH \cdot [CH_2]_7CO_3H$ , which is a colourless substance, not much more explosive than the other ozonides and has the same general chemical properties.

Elaidic acid yields a normal and a per-ozonide which seems to differ little if at all from those of oleic acid.

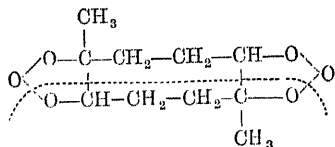
Citronellol yields a similar ozonide, per- and superperozonide (Harries and Himmelmann, Ber. 1908, 41, 2187).

**Cholesterol ozonide**  $C_{27}H_{46}O_5$ , which is probably an oxozone derivative, forms a very stable white powder and, when boiled with water, yields hydrogen peroxide, aldehydes and much resinous products. Similar ozonides of cholesterol derivatives have also been obtained (Diels, Ber. 1908, 41, 2596; Langheld, *ibid.* 1023).

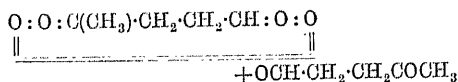
The most interesting application of the formation of ozonides to the elucidation of the structure of a compound is perhaps that of rubber. When the latter is treated with 5.5-6 p.c. of ozone, in chloroform solution for one hour for every gram, and the product evaporated *in vacuo* below  $20^\circ$  and the residue purified in the usual way, a *diozonide*  $C_{10}H_{16}O_6$  is formed as a yellow thick oil. It dissolves in various solvents yielding, not colloidal, but ordinary solutions, and when boiled with water or distilled with steam it yields laevulic aldehyde and acid, and laevulic aldehyde superoxide. The formation of this ozonide and its decomposition products, together with the fact that when heated, rubber yields, amongst other products, isoprene and dipentene, has led Harries to give the following formula to rubber



which agrees very well with its other known reactions. With ozone, it would form the diozonide

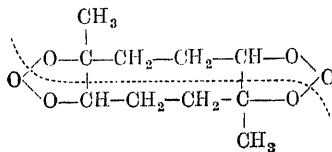


which, on decomposing, breaks at the dotted lines and therefore yields



Laevulic aldehyde diperoxide is readily transformed to the aldehyde in the presence of steam, consequently the laevulic aldehyde is present in large quantity (Harries, Ber. 1905, 38, 1195).

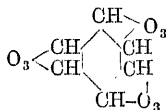
Gutta-percha gives a diozonide which seems identical with rubber diozonide, but on decomposition with water, it yields much less aldehyde and more acid: its decomposition has therefore been represented as taking place chiefly thus



yielding

$OC(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH : O : O : OCH \cdot CH_2 \cdot CH_2 \cdot C \leq O$  the latter readily being transformed into acid. The difference in behaviour of the two ozonides on decomposition is assumed to be due to some form of stereo-isomerism (*ibid.* 3985).

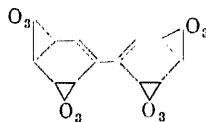
**Benzene triozonide or ozobenzene**



is formed by passing absolutely dry 5 p.c. ozone into dry benzene at  $5^\circ-10^\circ$  for about 2 hours. It is stable in dry air at the ordinary temperature and forms a white amorphous mass which, if quite pure, becomes crystalline when treated with water at  $0^\circ$ . It is soluble in acetic acid but not in other organic solvents. When warmed quickly it explodes violently, and when treated with water it yields chiefly glyoxal  $OHC \cdot CHO$  and some glyoxylic acid which probably results from the oxidation of the aldehyde with the hydrogen peroxide formed in the first reaction. These reactions show almost conclusively that benzene has three double linkings and that Kekulé's structural formula for benzene is correct.

Only the decomposition products of the tri-ozonides of toluene *o*- and *m*-xylene and of mesitylene have been obtained.

**Diphenyl** forms a *tetraozonide*



obtained as a crystalline mass, which explodes violently when heated. The fact that two more ozone molecules are not added at the double linkings is probably due to steric hindrance.

**Naphthalene**, when strongly cooled and submitted to the action of ozone, yields a crystalline

*diozonide*, thus , indicating that, in

all probability, only one of the rings has the benzene or Kekulé structure, whilst the other, in the non-aromatic form. When treated with water it yields phthalic aldehyde  $C_6H_4(CHO)_2$ , phthalic acid, glyoxal, and glyoxylic acid.

**Phenanthrene** when treated similarly also forms a diozonide  $C_{14}H_{10}O_6$  having similar properties to the naphthalene diozonide.

**Tetrahydrobenzeneozonide**  $C_6H_{10}O_3$ , obtained by passing ozone into a chloroform solution of

the unsaturated hydrocarbon, forms elastic lumps, sparingly soluble in most solvents, and when boiled with water yields *n*-adipic acid and a little aldehyde.

*Diadipic acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , a diozonide



which, on purification, forms a clear syrup with a characteristic smell. It is comparatively stable, but sometimes explodes with great

violence (Harries and Neresheimer, Ber. 1906, 39, 2846).

*Literature.* Harries, Annalen, 1905, 343, 311; *ibid.* 1910, 374, 288; Ber. 1912, 45, 809; Lebedeff, J. Russ. Phys. Chem. Soc. 1910, 42, 949; Drugman, Chem. Soc. Trans. 1906, 939; Dyckerhoff, Autoxydation organischer Stoffe, Inaug. Dissert. Karlsruhe, 1910; Valcur, Action de l'Ozone sur les composés Organique, Paris, 1909.

## P

**PACHNOLITE** (παχνή, rime). A fluoride of aluminium, calcium, and sodium, occurring as an incrustation or efflorescence on cryolite. It is regarded by Knop as a hydrated cryolite in which two-thirds of the sodium are replaced by calcium (A. Knop, Annalen, 127, 61).

*Composition.*—

Al.	Ca.	Na.	F.	H <sub>2</sub> O.
13.43	17.84	10.75	49.78	8.20=100.00

**PACKFONG** or **PACKTONG**. A Chinese name for nickel silver, and of a similar

**PACO** or **PACOS**. A Peruvian term for a ferruginous earth or ore containing small quantities of metallic silver.

**PAEONINE** (*Red Coralline* or *Aurine R.*) v. **AURINE**.

**PAINT OILS.** Under this term are comprised those vegetable oils which are used as vehicles for applying pigments to the surface of bodies, either as a preservative or for decorative purposes. Only the vegetable drying oils are useful; the paint oil, *par excellence*, is linseed oil. The semi-drying oils, such as cotton seed oil and maize oil, are unsuitable as paint oils. Nor is soya bean oil suitable as a paint oil, although when the price of linseed oil was high it was largely used as a substitute for linseed oil or to adulterate linseed oil. Fish oils, which are used as adulterants to an enormous extent, are unsuitable as paint oils, notwithstanding frequently made statements to the contrary. Adulteration with rosin oil is practised on an extensive scale, although more easily recognised than adulteration with animal and vegetable oils of somewhat lower iodine value than linseed oil. Oil extracted by solvents is not suitable as a paint oil. J. L.

**PAINTS.** *Definition.*—Coloured mixtures, usually liquids, with which suitable surfaces can be coated by a brush or other means. The coverings formed may be dull or lustrous, and often act as preservatives of the surfaces. Paints differ from varnishes in that they impart lustre, and in the absence of this property are but enamel paints and various special products are of exceptional composition. Ordinary paints consist essentially of three parts, the *pigment*, the *medium* or vehicle, and the *drier* or siccative. Paints manufactured for particular uses, such as luminous paints, anti-corrosive paints, and waterproof paints, contain other components of the most diverse kinds.

Surfaces only are covered by paints: dyes

stain throughout. This distinction is maintained in the present article, from which is excluded the consideration of dyes. The term 'pigment' will be confined to those substances to which paints owe their colours; mostly dry powders, finely diffusible but insoluble in the binding and thinning media employed. 'Paint' will be employed in reference to the combination of pigment and medium, ready for use by the painter. Pigments will first be described, and then the vehicles by which these pigments are converted into paints. Driers come next in order: lastly, paints themselves.

**Pigments.** *Definition.*—Finely divided insoluble coloured powders, yielding paints when intimately mixed with suitable media.

*Origin.*—Pigments are obtained from mineral, vegetable, and animal sources, chiefly the first-named. Inorganic pigments comprise minerals and manufactured products, mostly metallic salts or oxides: such pigments are usually more permanent than those of vegetable or animal origin.

*Characters.*—1. Body or opacity, *i.e.* the property of completely covering and concealing the surface beneath. 2. Covering or spreading power; the extent to which a pigment can be spread over a large surface. 3. Drying quality, when combined with a medium to form paint. 4. Durability or permanency. 5. Tint. 6. Shade.

Pigments may be of all degrees of opacity, and they vary in density and in the state of their particles. Some are opaque and amorphous; others are crystalline and translucent or transparent. The higher the density and opacity of a pigment, the greater is its body. Crystalline powders, however impalpable, have less opacity than amorphous powders, hence the superiority of the latter, as regards covering power. The drying quality of a pigment (in an oil paint) depends upon its power of oxidising or promoting the oxidation of the medium with which it is mixed: this property is possessed in a much greater degree by some pigments than by others and siccatives must be added when the pigment is known to be deficient in this characteristic. Permanency is tested by the power of the pigment, when made into paint, of resisting the action of light, moisture, fetid gases, acid and alkaline vapours, exposure to the atmosphere, &c. In special circumstances, as for the colouring of a lime-plastered surface, for fresco work, or the like, pigments must be unaffected

by, or 'fast' to, lime. As a rule, pigments are more durable when mixed with oil than when used in aqueous media. Instances are known of pigments in admixture exercising a detrimental influence upon one another. In oil media, this action is rarer than has been supposed: but an example is the darkening of the green pigment made by mixing cadmium yellow with emerald green, the last-named being, to a slight extent, dissolved by the linseed oil and therefore enabled to react upon the cadmium sulphide. Tint depends upon chemical composition, molecular constitution, physical condition, and the mode of production. The exact shade is a resultant of many niceties of detail during the processes in the colour factory. In a case, for example, where the pigment has been precipitated from solution, the shade will vary with the amount of care devoted to the washing of the precipitate—a very small percentage of impurity being the cause of a marked difference in quality. The degree of subdivision of a pigment also has a most important influence on the shade. Of great weight are the extent of dilution of the solutions, and the amount of

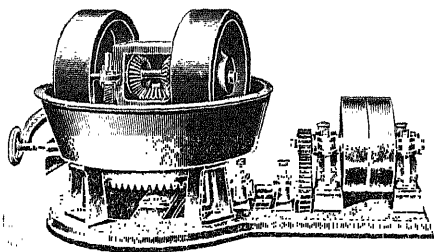


FIG. 1.

Positive Driven Edge Runner Mill (Brinjes and Goodwin, Ltd.).

efficient agitation, or mixing. The precipitated pigments are usually finer and brighter in shade, in direct proportion to the dilution of the solutions employed.

*Preparation.*—The pigments of commerce are so numerous that it will be impossible to describe the manufacturing processes by which most of them are obtained; but the important operation of grinding must be mentioned. All pigments must be in an extremely fine state of division. The colours used by house-painters and paper-stainers are pulverised and mixed by paint-grinders, while the more numerous and brilliant pigments used in the fine arts are ground by hand. Formerly, most pigments were ground by hand on a grinding stone with the aid of a muller, but the unhealthy and dangerous nature of the operation, especially when orpiment, white and red leads, chrome yellow, and many other important pigments, were treated, led to the introduction of colour mills, in which larger quantities of pigments can be ground and mixed in covered vessels, so that the risk to the workmen is very greatly lessened.

*Colour grinding.*—On the larger working scale, pigments are *dry-ground* chiefly in under-driven edge-runner mills: on a somewhat

smaller scale, conoidal mills, which are especially serviceable for materials composed of soft fragments, may be used. The centrifugal mills known as 'disintegrators' are exceedingly convenient. Fig. 1 shows one of the positive-driven

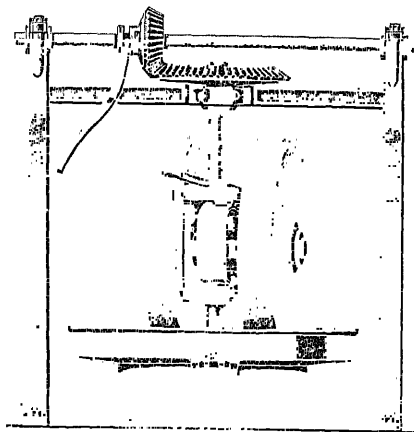


FIG. 2.

Edge Runner Mill, over Driven (Brinjes and Goodwin, Ltd.).

edge-runner mills, manufactured by Brinjes and Goodwin, Ltd., of Whitechapel. In this machine, the movement around the pan, and the revolution of each stone upon its axis, are caused by special gearing. Other types of edge-runner

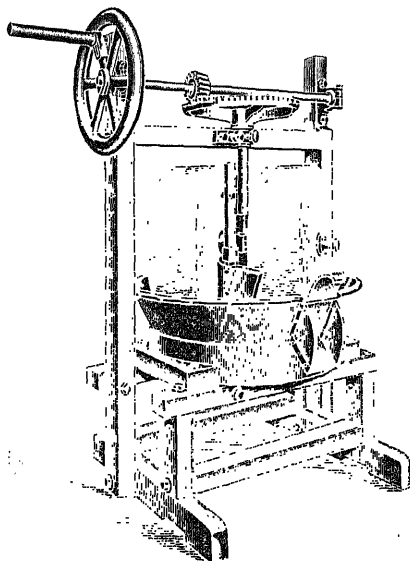


FIG. 3.

Edge Runner Mill, Top Driven (Bryan Corcoran, Ltd.).

mills, top-driven, are represented in Fig. 2 (same makers) and Fig. 3 (Bryan Corcoran, Ltd., London). The fourth illustration shows an under-driven mill of a similar description

(Wm. Gardner & Sons, Ltd., Gloucester). The bottom-driven type of mill is for colour-grinding preferable to, and now more generally used than, the top-driven kind. The bed and runners of these mills for colour-making should be of

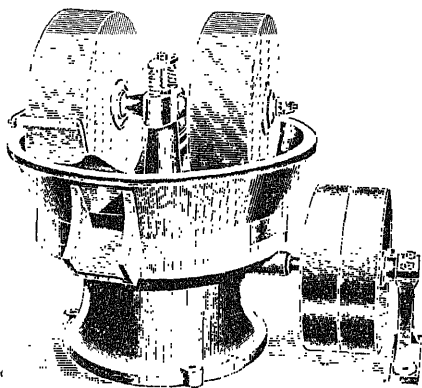


FIG. 4.

Underdriven Edge Runner Mill (Wm. Gardner & Sons, Ltd., Gloucester).

granite. When large fragments of highly resisting materials have to be dealt with, a less rigid form of mill than the positive-gear is to be recommended.

A conoidal mill, supplied by Bryan Corcoran,

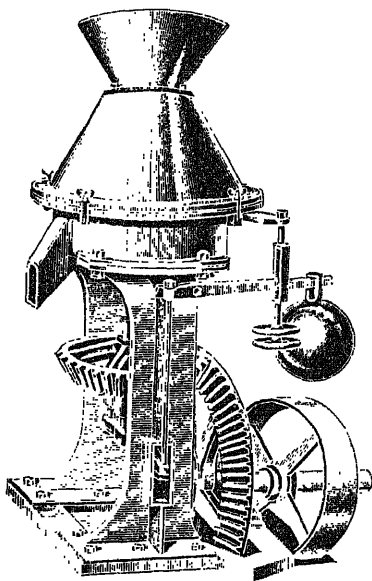


FIG. 5.

Conoidal Mill (Bryan Corcoran, Ltd.).

Ltd., of Mark Lane and Whitechapel, is shown in Fig. 5, and in Fig. 6 is represented a disintegrator (Wm. Gardner and Sons, Ltd., Gloucester).

Pigments may be *wet-ground* in a levigating

edge-runner; in a pulveriser of special construction, such as the 'Alsing' pulveriser; or, if the required output be small, in a levigating flat-stone mill. Edge-runner mills are mostly used.

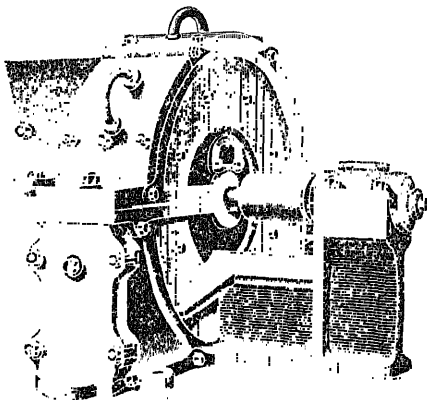


FIG. 6.

A Disintegrator (Wm. Gardner & Sons, Ltd.).

*Paint grinding.*—The older type of machine for the grinding of *mixed paints* was the ordinary flat-stone mill (Fig. 7), but the triple roller grinding mill (Fig. 8) has almost entirely superseded it.

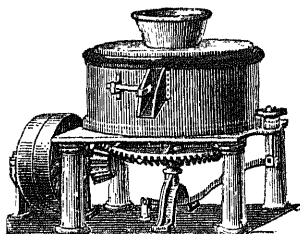


FIG. 7.

Flat Stone Mill (Brinjes and Goodwin, Ltd.).

*Paint mixing*, which precedes the grinding, is usually conducted either in a vertical mixer similar to that shown in Fig. 9, or in a hori-

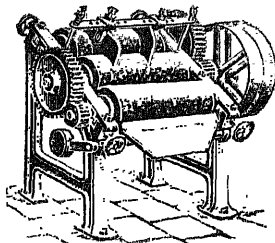


FIG. 8.

Triple Roller Grinding Mill (Brinjes and Goodwin, Ltd.).

zontal mixer, which may be of the kind depicted in Fig. 10. In certain cases, however, as in the mixing of zinc paint, a positive-gear edge-runner mill (Fig. 1) is the best to use. If a

volatile medium be necessary, as in the production of enamels, a conoidal mill (Fig. 5) may conveniently be substituted.

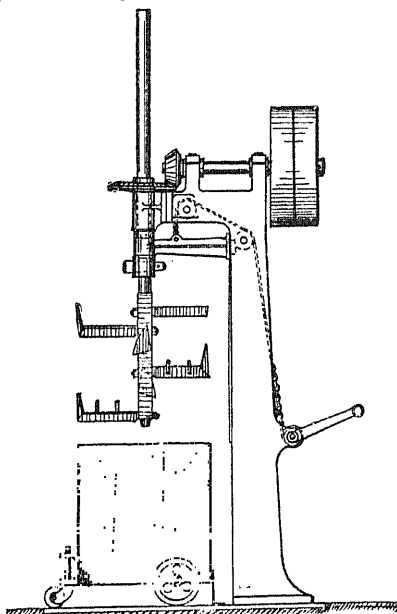


FIG. 9.

Ready-mixed Paint Mixer, with De Gendreau Stirrers (Brinjes and Goodwin, Ltd.).

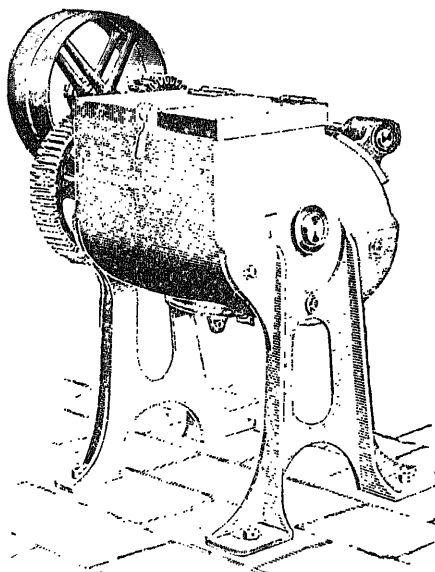


FIG. 10.

Geared Horizontal Mixer (Brinjes and Goodwin, Ltd.).

The more important and widely used pigments, classified according to colour, will next be briefly described. For further details *v.* art. **PIGMENTS**.

### WHITE PIGMENTS.

**White Lead** (*Céruse, Cerussa Alba, Blanc de Plomb, Kreams white, Bleiweiss*). For manufacture *v.* **White lead**, art. **LEAD**.

**Characters of good white lead.**—A perfectly amorphous white pigment, possessing great opacity, density, and covering power, and the property of drying rapidly when mixed with linseed or a similar oil, and exposed to the air. The hydroxide combines with the oil, forming a white elastic coating or paint; but lead hydroxide alone would give little opacity, which is imparted by the carbonate present. The latter forms an emulsion with the oil, of extreme opacity. Both, then, are essential.

**Additions to, and diluents of, white lead.**—Barium sulphate and chalk principally; but calcium sulphate, clay, lead sulphate, &c., are also added. Most of the cheaper so-called white lead in the market contains an admixture of some other comparatively cheap pigment. Certain of these are themselves used as white pigments of inferior quality.

**Substitutes for white lead.**—The chief, if not the only, objections to white lead as a pigment are its poisonous character and its tendency to darken in the presence of sulphuretted hydrogen.

Many other pigments are used as substitutes, but all are inferior to white lead in body. Sulphate of lead (*Mühlhausen white*); oxychloride of lead (*Pattinson's white*); a mixture of lead sulphate, barium sulphate, zinc carbonate (*Freeman's*); 'sublimed white lead';

(lead sulphate 75 parts, lead oxide 25 parts, and zinc oxide 5 parts); 'standard zinc lead white' (lead sulphate 50 p.c., zinc sulphate 0.40 p.c., zinc oxide 49.55 p.c.); zinc oxide; zinc sulphide; and a mixture of oxide, sulphide, and sulphate of zinc, have been manufactured for this purpose. A calcined mixture of 70.5 p.c. of barium sulphate with 29.5 p.c. of zinc sulphide, prepared by precipitating a solution of barium sulphide with zinc sulphate, washing, pressing, drying and 'firing' the resulting precipitate, constitutes the pigment known as *Lithopone, Orr's white, Charlton white, or Beckton white*. One of the most useful and valuable substitutes for white lead, lithopone, is quite unaffected by sulphuretted hydrogen, is possessed of great permanency, and fineness of texture. It is not injurious to health than white lead and yields an excellent oil-paint. *Sulphopone* is a similar pigment prepared from zinc sulphate and calcium sulphide. The addition of calcium sulphate is stated to counteract the discolouring effect of light and air upon lithopone. Among other white lead substitutes may be mentioned basic lead sulphate; oxide and silicate of zinc; zinc oxide with sulphide or chloro-sulphide of lead; mixtures of barium sulphate and calcium sulphate with zinc oxide, and basic chloride of zinc.

**Other white pigments.** The white pigments of commerce are known by a great variety of names. *Flake white, Berlin white, silver white, and Kreams white* are names applied to very fine and pure varieties of white lead. *Venice, Hamburg and Dutch whites* are mixtures

of white lead and barium sulphate in different proportions. *Blanc fixe*, *Baryta white*, *fast white*, and *Permanent white* are barium sulphate. *Strontium* or *Strontian white* is sulphate of strontium. Magnesia ( $MgO$ ) and magnesium carbonate ( $MgCO_3$ ) constitute *Magnesia whites*. *Spanish white* or *Paris white*, is *whitening*, or *whiting* ( $CaCO_3$ ). Whitening, gypsum, kaolin, French chalk, asbestine, infusorial earth, &c., are used in mixed paints as 'extenders' or 'fillers,' and some of them, with lime, are employed as painting grounds, rather than as pigments. *Zinc white* and *Chinese white* are names given to zinc oxide. First employed on a commercial scale by Leclaire, c. 1847, this beautiful pigment is increasing in favour as a constituent of ordinary paints, and for the production of enamels, white oil-cloths, and the like. Zinc white possesses very fair covering power, though less than flake white: it is not visibly affected by sulphuretted hydrogen. It can be used with oil- or water-media—especially well with the last-named, and is non-poisonous. In an oil vehicle it dries far less rapidly than lead white. Admixture with calcium sulphate is alleged greatly to enhance the spreading power of zinc oxide. Carbonate of zinc has been employed as a pigment, but not very successfully. *Pearl white* is basic nitrate of bismuth [ $Bi(NO_3)_3 \cdot 2Bi(OH)_3$ ], but the name is also used in connection with a lead white, tinted with indigo or some other blue pigment. Yet another *Pearl white* is bismuth carbonate [ $Bi_2O_3 \cdot Bi_2O_3 \cdot H_2O$ ]; and basic carbonate of lead [ $Pb_3O_4 \cdot PbO$ ] is occasionally called *Flake white*. Whites of tin, cadmium, mercury, arsenic, tungsten, and antimony have all been tried, but without permanent success. Antimony white, however, is said to have considerable covering power. The oxide,  $Sb_2O_3$ , and powder of  $As_2O_3$ ,  $As_2S_3$ , are both used, but these are not permanent on exposure.

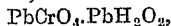
#### YELLOW PIGMENTS.

*Yellow ochres*, *Terra di Siena*, *Stone yellow*, *Roman ochre*, *Mineral yellow*, *Oxford ochre*, *Golden ochre*, &c., are ferric oxides, containing varying percentages of water. *Mars yellow* is an artificial preparation of similar composition. A pigment called by the same name, also termed *Silerin yellow*, is  $Fe_2(CrO_4)_3$ . *Chrome yellow* is  $PbCrO_4$ ; also  $PbCrO_4 \cdot PbSO_4$ ; and  $PbCrO_4 \cdot 2PbSO_4$ . Pale and greenish shades contain citrate or tartrate of lead, and sometimes also sulphate, as well as lead chromate. *Orange chrome yellow* is  $PbCrO_4 \cdot PbO$ . *Cologne yellow* is  $PbCrO_4$ ,  $PbSO_4$ , and  $CaSO_4$ . (These yellows possess considerable body, but are affected by sulphuretted hydrogen.) *Strontium*, *Barium*, and *Zinc yellows*,  $SrCrO_4$ ,  $BaCrO_4$ , and  $3(ZnCrO_4) \cdot K_2Cr_2O_7$  (durable, but have little body). Barium chromate (*Lemon yellow*, *Yellow ultramarine*) is the most permanent of these pigments. *Bismuth yellow*, also a chromate (not permanent). *Cadmium yellow*,  $CdS$ , durable, of fairly good body, and unaffected by sulphuretted hydrogen. True *Naples yellow*,  $PbO \cdot Sb_2O_5$  (permanent in oil). Cadmium sulphide, and a pale yellow ochre, have been sold under the same name. *Montpellier*, *Cassel* ( $PbCl_2 \cdot 7PbO$ ), *Turmer's*, *Turin*, *Verona*, and *Paris yellows*, oxy-

chlorides of lead (not lasting). *King's yellow* or *Orpiment*,  $As_2S_3$  (unstable). *Wolfram*, *Vanadium*, *Uranium*, *Thallium*, *Palladium*, *Tin*, *Antimony*, and *Platinum yellows* (most unstable and little used). *Indian yellow* or *Purree*,  $C_{45}H_{72}O_{11} \cdot 5H_2O$ , from mango-leaves. A beautiful but variable pigment. *Madder yellow*, *Italian pink*, *Brown pink*, &c. (vegetable: non-durable—bleached on exposure). *Gamboge* (a resin: unstable). *Aureolin*, occasionally used, or *Indian yellow*, potassium cobaltinitrite,  $K_3Co_2(NO_3)_{12} \cdot 2H_2O$  (fairly permanent).

#### RED PIGMENTS.

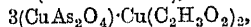
*Vermilion*, *Cinnabar*,  $HgS$  (moderately permanent in oil: alterable in water-colour): too expensive for use in ordinary paints. *Minium*, *Red lead*,  $Pb_3O_4$  or  $PbO \cdot Pb_2O_3$  (not permanent), *Light red*, calcined yellow ochre; *Indian red*, *Venetian red*, *Rouge*, *Colcohar*, *Bole*, *Caput mortuum*, &c.: ochres (all durable colours). Some of these pigments are artificially obtained by calcining ferrous sulphate. *Chrome red* or *Austrian cinnabar*, basic lead chromate,



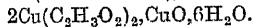
and *Chrome oranges*, mixtures of normal and basic lead chromates (all unstable). *Realgar*,  $As_2S_3$ , arsenic sulphide. *Antimony vermillion*, antimonyoxysulphide,  $Sb_2S_5 \cdot O_3$ . *Palladium red*, ammonio-chloride of palladium, and *Brilliant scarlet*, mercuric iodide (very unstable), have been used. *Vandyke red* is copper ferrocyanide,  $Cu_2Fe(CN)_6$ . The cobalt reds are too costly for general use. *Madder lakes* (vegetable colours on mineral bases; unreliable). *Carmine lake* (of animal origin—from *Coccus cacti*; a beautiful colour, but not permanent).

#### GREEN PIGMENTS.

*Terre verte*, an impure ferric silicate (permanent, but deficient in body when used as an oil-colour). Many salts of copper have been used as green pigments. Among the best known of the copper greens are *Malachite*, *Mountain green*, or *Green verditer*, hydroxycarbonate of copper,  $CuCO_3 \cdot CuH_2O_2$ , *Schweinfurt* or *Emerald green* (acetoarsenite),



*Brunswick green* (oxychloride),  $CuCl_2 \cdot 3CuO \cdot 4H_2O$ , and *Verdigris* (basic acetate),



*Scheele's green* is a basic arsenite of copper, now but little used. *Mitis*, *Vienna*, and *Kirchberger* are other names for *Scheele's green*. *Bremen green*, *Prussian green*, *Cobalt green* (stannate), and *Mineral green*, are other copper pigments. All are darkened by sulphuretted hydrogen, and most are very poisonous.

Mixed greens: *Brunswick green* (another kind), *German green*, *Hooker's*, *Leaf*, *Milroy*, and *Silk-greens* are mixtures of various yellow and blue pigments, and can be dismissed as of very inferior quality.

*Pannetier's*, *Arnau-don's*, and *Verdigris* are emerald greens are hydrated sesquioxides of chromium, with phosphate or borate of chromium. *Viridian*

chromium greens are Casali's, Dingler's, and Schmitzer's products. *Rinmann's green*, *Cobalt green*, or *Zinc green*, a compound of oxide of cobalt and oxide of zinc. *Titanium*, *Vanadium*, *Uranium*, *Manganese*, and *Molybdenum* also occasionally met with as ultramarine is a product of the manufacture of There are many unstable green lakes of vegetable origin, such as *Chinese green*, *Iris green*, and *Sap green*, but they are of little or no value. Some of the green lake pigments prepared from the coal tar colours, however, possess considerable covering power and a measure of fastness to light.

#### BLUE PIGMENTS.

*Prussian blue*, *Berlin blue*, *Chinese blue*, &c.,  $\text{Fe}_3(\text{CN})_{12}$  (liable to change). *Soluble Prussian blue*, of inferior quality to the preceding, is  $\text{K}_2\text{Fe}(\text{CN})_{12}\cdot\text{Fe}_2$ . *Antwerp blue* is a light-tinted variety of Prussian blue. *Indigo*, or *Indigotin*,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$  (vegetable; fades on exposure). *Native ultramarine*, pulverised lapis lazuli (an excellent and stable, but costly colour). *Artificial ultramarine*, probably  $\text{Na}_4(\text{Na}_2\text{Al})\text{Al}_2(\text{SiO}_4)_3$  (Brügger and Backström) a compound of silicate of aluminium and sodium, with sulphide of sodium; suggested by Gmelin, in 1827, and made by Guimet in 1828. Less expensive than native ultramarine, and nearly equal to it as a pigment. *Bohemian blue*, *Thénard's blue*, phosphate and aluminate of cobalt. *Cobalt blue*, *Gahn's ultramarine*, aluminate of cobalt. *Cyanine*, *Leitch's blue*, a mixture of cobalt blue and Prussian blue. *Small*, *Zaffre*, *Royal*, and *Saxony blues*, glasses coloured by cobalt oxide. *Caruleum*,  $3(\text{SnO}_2\cdot\text{CoO})+\text{SnO}_2$  (stannate of cobalt). The cobalt colours lack somewhat in body and fastness. *Copper blues*, carbonates, and salts of copper, are of little value.

#### BROWN PIGMENTS.

*Vandyke*, *Rubens*, *Cassel*, *Ulm*, and *Cologne browns*: some of these are partly vegetable, and are prepared from peat, cotton, soot, &c.; bituminous matter is often present. Several different pigments are known as *Vandyke brown*. Only those prepared by calcining highly ferruginous brown ochres, or consisting of a dark-tinted form of colcothar, are permanent. The variety of Vandyke brown, consisting of a bituminous earth, is far less durable. *Burnt sienna*, *Brown terre verte*, *Raw* and *burnt umber*, *Cappagh brown*, and *Mars brown*, are earths or ochres, raw or calcined. Most of them are durable and reliable pigments. Other browns are *Prussian brown*, made by calcining Prussian blue; *Madder brown* (of vegetable origin, and liable to fade); *Bistre*, a bituminous brown; *Asphaltum*; and *Mummy*. The last three also are untrustworthy and fugitive.

#### BLACK PIGMENTS.

*Ivory black*, *Bone black*, *Lamp black*. These are more or less pure carbon, and the names are self-explanatory. *Indian ink* consists of very fine lamp black, together with gelatin and a

perfume (*n. INDIAN INK*). *Blue-black*, *Frankfort black*, or *Drop black* is made from vine twigs, ivory cuttings, bone shavings, peach stones, and other organic materials, which are calcined until complete charring is effected. After grinding, the black so obtained is made up with glue and water into pear-shaped drops for sale. *Manganese black* is native peroxide of manganese. All these black pigments are very durable. *Sepia* is a brownish-black pigment derived from the ink-bag of *Sepia officinalis*: it is alterable by sunlight, but less so than *Vandyke brown*, &c.

Of the above-mentioned pigments, only a few (chiefly the ochres, lamp-black, red lead, white lead, zinc white, baryta white, Prussian blue, chrome yellow, orange and red, vermilion, and the commoner copper greens) enter into the constitution of the paints used by decorators and house-painters; white lead is nearly always the base, and is largely in excess of the other pigments present, which are technically called the 'stainers.' The finer varieties of these colours and many of the other pigments, are used habitually or occasionally by artists. Of pigments not named in this article, there are many which are simply of inferior quality, with no good qualities to recommend them.

As regards durability, it may shortly be stated that all the compounds of copper, lead, and bismuth, and some mercurial pigments, darken more or less, when exposed to air containing sulphuretted hydrogen gas. Some of the colours which are partly or entirely of organic origin fade on exposure, by a process of oxidation. On the other hand, pigments which are not affected by foul gases, the barium and zinc whites, for example, have unfortunately, for the most part, less covering power than the majority of lead, copper, and other changeable pigments. Great circumspection must, therefore, be exercised in the choice of a pigment, whether for artistic or ordinary work. As a rule, pigments are less fugitive in oil-media than when mixed with the usual water-colour vehicles. Church (*The Chemistry of Paints and Painting*, 1901) classifies artists' pigments, according to their stability in oils, as shown in the table, page 74.

To adapt this table to water colours, the pigments marked X must be relegated to class III.; while Indian ink, bistre, and sepia may be added to the table. But the two last named must be placed in class III.

The following examples of carefully chosen palettes are quoted from Church's work, just cited: (a) for oil-painting, flake white, yellow ochre, cadmium yellow, aureolin, vermilion, madder carmine, ultramarine, viridian, Cappagh brown, and ivory black: (b) for water-colours, Chinese white, yellow ochre, cadmium yellow, aureolin, red ochre, madder carmine, ultramarine, viridian, Mars brown, and Indian ink.

**Media or Vehicles.** *Definition.*—The fluids or other materials with which pigments are intimately mixed for the purpose of painting. For oil-paints, the vegetable drying or siccative oils are employed, and for water-colour paints, size, honey, glycerol, and the like, are in use. These are added to the oil as 'thinning' agent, and partly to accelerate somewhat the drying of the paint. Benzene,



Class I. Truly permanent.	Class II. Somewhat changeable.	Class III. Untrustworthy.
Baryta white.	Aureolin.	King's yellow.
Zinc "	Baryta yellow.	Yellow madder.
× Flake "	Indian "	Brown pink; yellow lake.
Yellow ochre.	Strontia "	Gamboge.
Raw sienna.	× Chrome "	Zinc chromate.
× Naples yellow, true.	Madder carmine.	Crimson lake.
× Cadmium "	Rubens' madder.	Carmine and burnt carmine.
Cadmium orange.	Rose "	Indian lake.
× Vermilion, artificial.	Madder red.	Scarlet "
Vermilion, native.	Purple madder.	Purple "
Indian red.	Mars violet.	Violet carmine.
Light "	Emerald green (Schweinfurt g.)	Verdigris.
Venetian red.	Terre verte.	Sap green.
Red ochre.	× Malachite.	Green vermilion, etc.
Cobalt violet.	Smalt.	Indigo.
Manganese violet.	Prussian blue.	Blue verditer.
Viridian (emerald oxide of	Antwerp "	Blue ochre.
chromium, $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ).	× Madder brown.	Bituminous Vandyke brown.
Green oxide of chromium,	Cologne earth.	
$\text{Cr}_2\text{O}_3$ .	Bitumen.	
Cobalt green.	Earthy Vandyke brown.	
Green Ultramarine.		
Ultramarine.		
Artificial ultramarine.		
Cobalt.		
Cœruleum.		
Burnt sienna.		
Raw and burnt umber.		
Cappagh brown.		
Verona "		
Prussian "		
Ivory black.		
Charcoal black.		
Lamp-black.		
Graphite.		

and turpentine substitutes, allied to petroleum spirit, are similarly used. In *tempera-painting* albuminous or gelatinous media are employed, and water-glass is the vehicle in *stereochromy*. Lime-water or baryta-water is used in *buon fresco*, and *fresco-secco* painting. In *pastel painting*, the bases for the pigments are whitening, and (sometimes) plaster of Paris, or kaolin. Beeswax was the medium in Greek and Egyptian *encaustic* work, and is employed in *spirit-fresco*. Other paint-media are occasionally made use of, and will be referred to presently.

**Oils.** These are chosen for their drying properties, or, in other words, their power of absorbing oxygen when spread in thin layers and exposed to the atmosphere; by this oxidation a film of a drying oil gradually becomes converted into a coherent coating of a hard, elastic, varnish-like substance.

*Linseed oil* is the most important and commonly used drying oil; it is met with in commerce under the names of *raw*, *refined*, *artists'*, and *boiled* oil. Raw oil is as expressed from the seeds. By agitation in lead-lined tanks with 1 p.c. of strong sulphuric acid, boiling with water or treatment with steam, and drawing off in settling-tanks from water and sediment, raw oil is converted into refined oil. Artists' linseed oil has been allowed to stand for weeks or months, then treated with litharge

and finally bleached by exposure. Other processes of refining are also used. Boiled oil has been heated in air to  $130^\circ$ , or thereabouts, and maintained at that temperature for a little while. Raw linseed oil possesses great drying powers, which are considerably enhanced by the operation of boiling. Boiled oil is therefore a most important article to the painter. The drying power of boiled oil is still greater if litharge or some other drier has been added during the operation of boiling. The drier appears to act as a carrier of oxygen to the oil, and a definite chemical compound of the metallic oxide with linoleic acid is at the same time formed (*v. OILS, FIXED, AND FATS; DRIERS*). Both raw and boiled linseed oil are used in the manufacture of *oil-paints*. For the more delicate *oil-paints*, the fine arts, refined and artist's oils are used.

Poppy, walnut, and hemp oils are also used in the manufacture of paints, particularly poppy, walnut, and hemp oils. These oils are, however, almost exclusively used by artists; and linseed oil holds its own as the most generally useful and applicable drying oil. Numerous additions to, and substitutes for linseed oil have been tried, among them mineral and resin oils, China wood oil (Tung oil), Niger-seed oil, cottonseed oil, and menhaden oil.

Artists in oil generally use media which

contain copal, amber, or some other resinous varnish, and a diluent, such as turpentine, in addition to the drying oil. A good artists' medium can be prepared by gently warming a mixture of linseed or poppy oil with strong copal varnish and a trace of bleached beeswax. A less satisfactory medium is 'megilp,' composed of linseed oil and mastic varnish. Such media are added to the mixed colours by the artist.

The vehicles for water-colour paints need no description; they are, chiefly, isinglass, size, gum-water (gum-arabic, gum-tragacanth, and gum-senegal are all used), honey, dextrin, and glycerol. Of the gums, gum-senegal is the most suitable. Dextrin is less adhesive and less brittle than gum. An alcoholic solution of honey-lavulose is preferable to honey itself.

The various 'pastes,' 'fritts,' and 'glazes,' used for ceramic ware, enamels, painted glass, and the like, are outside the scope of this article (*v.* FRITTS AND GLAZES; POTTERY).

**Driers or Siccatives.** The effect of these on the drying oils has been referred to. The driers mostly employed are litharge, acetate of lead, resinates of manganese and lead, manganese dioxide, and manganous borate. Manganese oxalate, manganese linoleate, calcium borate, zinc borate, zinc oxide, zinc sulphate, burnt alum, lime, red lead, and ferric oxide are sometimes used. 'Terebinies' or 'liquid driers' are solutions of certain of the above-named metallic organic compounds in linseed oil and turpentine. White lead itself has considerable siccativ power; this is one reason why it is so especially useful a pigment. The 'driers' of turpentine are commonly sold ready ground in oil. They must be used with care, as they sometimes detract from the delicacy of the colour with which they are mixed; and for this reason the use of driers should be avoided as much as possible in paints intended for 'finishing coats.'

**Paints.** The mixed colours, ready for use. Common oil-paints consist of the pigments (generally white, lead or a substitute, such as lithopone, together with small proportions of the desired 'stainers'), ground with oil in the paint mill to a thick paste, and mixed with 'driers.' They are sometimes manufactured and supplied as 'ready-mixed' paints (in which the painting of comparatively small articles can be effected by the simple operations of dipping and subsequent draining), but usually require 'thinning down' with oil of turpentine to the required consistency. The oil for outdoor work is usually boiled oil; while for indoor painting pale linseed oil is frequently used, together with a larger proportion of driers. The smaller the quantity of oil used, the greater is the ultimate hardness and the less the lustre of the paint. Distemper painting, for absorbent surfaces, such as plaster, necessitates the application of a 'priming,' consisting of white lead, or, very commonly, zinc oxide, ground in water and mixed with size. There is little to specify in reference to artists' oil-paints, excepting that they consist, or should consist, of pure pigments very finely ground in, and intimately mixed with, oil of the best quality, no base, such as white lead, being present. The proportion of oil used varies with the pigment, and ranges from less than 20 parts

per 100 of pigment, for materials such as lead and zinc whites, to over 175 parts per 100 for colours such as raw sienna, burnt sienna, and the like. Artists' water-colour paints are met with in the forms of cakes, pastilles, and tube-colours. Cakes and pastille colours are usually made by grinding the pigments into a paste with a little glycerol, size, and gum-water; the paste is then compressed and dried at a moderate temperature. Such paints are ground on the palette with water before use. Tube or moist colours consist of the pigments made into a cream with honey, glycerol, &c. Glycerol is preferable to honey.

Many other kinds of paints besides those already mentioned are manufactured at the present time. The principal of these are the luminous, fireproof, damp-resisting, anti-corrosive, water, washable, and enamel paints; their composition is very varied, and only a few short notes can be included in reference to them.

**Luminous paints** contain phosphorescent materials, such as strontium, barium, or uranium, and other salts. The mixtures are submitted to a calcination process, and combined with suitable pigments and media. Balmann's, Vanino's, Mourel's, and Lennord's luminous paints are well-known examples belonging to this class of products. They yield an especially powerful product.

**Fireproof paints.** These paints differ widely in composition, but asbestos is present in nearly all; and many contain alkaline silicates, borax, ground fluorspar, glass, and similar substances. A mixture of aluminium and sodium silicates is sold under the name of 'Fireproof Paint.'

**Water-proof or Damp-resisting paints.** These are made from crushed flint and asbestos, and contain numerous other ingredients enter into the composition of these preparations, either in addition to, or instead of, the ordinary constituents of paint. One of the most efficient waterproof paints on the market at the present time is stated to be the product known as "Inertol."

**Anti-fouling, Anti-corrosive, or Preservative paints,** for surfaces of iron, ships' bottoms, &c. Many of these paints contain resinous constituents, and resemble varnishes in this respect. Oxide of iron, pitch, shellac, colophony, tannin, silicates, &c., are common ingredients of these compositions. An emulsion of tar and clay is stated to be a highly protective coating for iron and timber.

**Water and Washable paints.** Ordinary 'distemper' cannot be washed, but many of the water-paints on the market at the present time are washable when dry. Some are 'silicate of soda' preparations; in others, butter-milk, or casein is used in association with the colours. The miscibility of some with water is brought about or promoted by the presence of soap, or by the partial saponification of the oil. Water-paints merely require mixing with water, and those which are described as waterproof should resist atmospheric influences as satisfactorily as oil-paints.

**Enamel paints.** These are brilliantly coloured decorative paints, yielding smooth and lustrous

coatings. Essentially they consist of oil varnishes, ground up with the finely divided pigments and thinned by spirit of turpentine. The high lustre of the painted surface is due to the large proportion of resins present.

Such miscellaneous materials as the so-called 'gold' paints and 'bronze' paints (of bronze-powders suspended in resinous varnishes, or in a solution of celluloid in amyl acetate and acetone); 'silver' paint (in which finely divided aluminium is the pigment); aniline-coloured aluminium paints; mica-scale paint; flexible paint; grease paints (tinted cosmetics); floor paints; roof paints; and the like, can receive but a bare mention here. Aluminium paint is now very extensively used.

For analysis of paints, *v. ANALYSIS*: also references below.

*Literature.*—J. Cameron, Oils and Varnishes, 1886; W. J. Russell and W. de W. Abney, Report . . . on the Action of Light on Water Colours, 1888; A. P. Laurie, Pigments and Vehicles of the Old Masters, Cantor Lectures, Soc. Arts, 1891-1892; J. Bersch, Die Fabrikation der Mineral-und Lackfarben, Wien, 1893; Evidence and Report, Departmental Committee on the Various Lead Industries, 1894; A. P. Laurie, Facts about Processes, Pigments, and Vehicles, 1895; R. Lemoine and C. du Manoir, Manuel Pratique de la Fabrication des Couleurs, Paris, 1898; G. H. Ellis, Analysis of White Paints, Chicago, 1899; F. H. Jennison, The Manufacture of Lake Pigments from Artificial Colours, 1900; J. Bersch (Trlr., A. C. Wright), The Manufacture of Mineral and Lake Pigments, 1901; A. H. Church, The Chemistry of Paints and Painting, 1901; J. C. Smith, The Manufacture of Paint, 1901; E. J. Parry and J. H. Coste, The Chemistry of Pigments, 1902; T. Oliver (ed.), Dangerous Trades, 1902; G. H. Hurst, The Painter's Laboratory Guide, 1902; E. G. Clayton, Some Analyses of Common Pigments, Chem. News, 85, (1902), 290; L. E. Andés (Trlr., A. Morris and H. Robson), Oil Colours and Printers' Inks, 1903; A. C. Wright, Simple Methods of Testing Painters' Materials, 1903; P. N. H. Luck, Painters' Oils, Colours and Varnishes, 1905; F. Diolé, Les Matières Premières employées dans la Peinture en Batiment, Paris, 1905; A. H. Sabin, The Industrial and Artistic Technology of Paint and Varnish, 1905; J. M. Thomson, The Chemistry of Artists' Colours in relation to their Composition and Permanence, Soc. Arts Jour. 54 (1905-6), 388-397; C. H. Hall, The Chemistry of Paints and Paint Vehicles, 1906; G. Zerr and R. Rübenkamp, Handbuch der Farben-Fabrikation, Dresden, 1906; A. P. Laurie, Oils, Varnishes, and Mediums used in the Painting of Pictures, Soc. Arts Jour., 55 (1906-7), 1-12; G. H. Hurst, Painters' Colours, Oils, and Varnishes, 1906; M. Toch, The Chemistry and Technology of Mixed Paints, 1907; J. G. Gentile (ed.), Die Farben-Fabrikation, Dresden, 1907; Deutsche Gesellschaft zur Förderung rationeller Malverfahren, Kommission zur Bekämpfung von Misständen in der Herstellung, im Handel und in der Verarbeitung der Farben und Malmaterialien, München, 1906; G. Petit (Trlr., D. Grant), The Manufacture and Comparative Merits of White Lead and Zinc White Paints, 1907; G. Zerr and R. Rübenkamp (Trlr., C.

Mayer), A Treatise on Colour Manufacture, 1908; C. D. Holley, The Lead and Zinc Pigments, 1909; J. C. Smith, Oxide of Zinc, Its Nature, Properties, and Uses, 1909; A. Eibner, Malmaterialienkunde als Grundlage der Maltechnik, Berlin, 1909; J. N. Friend, An Introduction to the Chemistry of Paints, 1910; W. G. Scott, White Paints and Painting Materials, Chicago, 1910; A. P. Laurie, Greek and Roman Methods of Painting, 1910; A. P. Laurie, Materials of the Painters' Craft, 1910. E. G. C.

**PALATINE ORANGE.** This colouring matter is the ammonium salt of tetranitro- $\gamma$ -diphenol. It is soluble in water, and dyes wool and silk orange in a bath acidified with acetic or sulphuric acid (Hummel, Dyeing of Textile Fabrics (1885), p. 401).

Tetranitro- $\gamma$ -diphenol  $C_{12}H_4(NO_2)_4(OH)_2$  is obtained by the action of fuming nitric acid on  $\gamma$ -diphenol or on benzidine, and melts at 220°: prolonged heating with concentrated nitric acid converts it into picric acid and oxalic acid (Schmidt and Schultz, Annalen, 207, 335).

**PALISANDER WOOD.** This name is now generally applied to one or more kinds of timbers that resemble rose-wood and are obtained in tropical South America and Mexico. The wood is lighter or darker violet brown or chocolate, and is marked by darker, often black, bands running with the grain. The actual origin of the timber is not known, but is attributed to the bignoniacous *Jacaranda brasiliensis* (Pers.) as well as to one or more species of the leguminous genera *Machaerium* and *Dalbergia*.

The name 'palisander wood' has apparently also been applied to an entirely different red dye-wood of unknown origin, obtained in

**PALLADIUM.** Sym. Pd. At. wt. 106.7. Occurs in all varieties of crude platinum and in many copper ores, especially in those which are nickeliferous and which are associated with pyrrhotine. It also occurs as an alloy with platinum or gold, especially in Brazil, and, in association with selenide of lead, in the Harz, in the form of hexagonal plates, although its crystalline form in other deposits is not known. Its principal source is the matte from the copper-nickel ores of Sudbury in Ontario. The total production of the United States, mainly from this source although partly from crude platinum, was over 2000 oz. in 1910.

Palladium has also been detected in a meteorite (Trotterelli, Gazz. chim. ital. 1890, 20, 611) and in the solar spectrum (Lockyer, Compt. rend. 1878, 86, 317).

*Preparation.*—Palladium may be precipitated as a double ammonium chloride from the mother liquor obtained after removing platinum and iridium (*v. PLATINUM*) (Wollaston, Phil. Trans. 1805, 95, 316). The pure metal may be obtained from the double salt by reducing the latter at a red heat in a current of dry pure hydrogen, after which the metal is cooled in a current of carbon dioxide to remove occluded hydrogen. The metal is also formed by the reduction of palladium chloride with formic acid or a formate. Mercuric cyanide precipitates palladium from neutral solutions as the white di-cyanide which yields the metal on ignition.

In either case the metal must be heated in hydrogen and then cooled in carbon dioxide.

*Literature.*—Bunsen, Phil. Mag. 1868, [iv.] 36, 253; Philipp, Dingl. Poly. J. 1876, 220, 95; Guyard, Compt. rend. 1863, 56, 1177; Leidie, *ibid.* 1900, 131, 888; Orloff, Chem. Zeit. 1906, 30, 714.

Palladium is a silver-white metal as hard as platinum but less ductile. It has a sp.gr. of 11.97 (Violle) and melts at 1546° (Waidner and Burgess, J. Soc. Chem. Ind. 1907, 1140). When heated to low redness in air, it becomes bluish, but it regains its white appearance at higher temperatures. At the melting-point of iridium, it boils and volatilises as a green vapour with partial oxidation.

It unites with fluorine and chlorine at a dull red heat, and superficially with iodine when treated with alcoholic iodine solution. Palladium is readily attacked by *aqua regia*, but less so by other acids. It unites with sulphur and selenium, less readily with phosphorus and arsenic, and with silicon at a white heat. It forms alloys with many metals.

Palladium has been employed for the graduated circles, &c., of philosophical instruments, and, to a small extent, in watch-making, and has been used for the electro-plating of parabolic mirrors on account of its silvery appearance and absence of change on exposure to impure air. It is also used for soldering platinum, but the bulk of the output is employed in the manufacture of dental alloys.

Palladium, in the form of palladium asbestos, is said to give excellent results when used as a contact substance in combustion analyses. It may be prepared for this purpose by precipitating a solution of pure palladium chloride in the presence of asbestos, by means of alkaline sodium formate (Jacobsen and Landesen, Ber. 1907, 40, 3217; Dennstadt, *ibid.* 3677).

Palladium, either in the form of sponge or black, has catalytic properties in a greater degree than platinum.

*Literature on the catalytic properties of palladium and of colloidal palladium.* Coquillon, Compt. rend. 1878, 87, 795; Phillips, Zeitsch. anorg. Chem. 1894, 6, 213; Lunge and Akunoff, *ibid.* 1900, 24, 191; Kraut, Ber. 1887, 20, 1113; Jahn, *ibid.* 1889, 22, 989; Zelinsky, *ibid.* 1898, 31, 3203; Bredig and Fortner, *ibid.* 1904, 3, 798; Paal and Roth, *ibid.* 1908, 41, 2273, 2282; *ibid.* 1909, 42, 1553; *ibid.* 1910, 43, 2684, 2692.

Palladium sponge or black would be employed on a commercial scale instead of or in conjunction with platinum if a sufficient supply were available.

Palladium absorbs various gases in quantities varying with its physical state (Cailletet and Collardeau, Compt. rend. 1894, 119, 830; Mond, Ramsay and Shields, Proc. Roy. Soc. 1897, 62, 290; Harbeck and Lunge, Zeitsch. anorg. Chem. 1898, 16, 50).

At ordinary temperatures, a palladium wire will absorb between 300 and 400 times its bulk of hydrogen and, when heated to redness in hydrogen, it absorbs nearly 1000 volumes and increases in bulk by nearly 10 p.c. This 'alloy' of hydrogen and palladium is permanent in air and *in vacuo* at ordinary temperatures, but yields up the whole of its hydrogen when

heated *in vacuo* (Mond, Ramsay and Shields, Chem. News, 1897, 76, 317; Dewar, *ibid.* 274; Fischer, J. Soc. Chem. Ind. 1906, 993).

'Palladium hydrogen' is a valuable reducing agent (Sabatier and Senderens, Compt. rend. 1892, 114, 1430; Ann. Chim. Phys. 1896, 7, 357, 383; Engel, Compt. rend. 1899, 129, 518; Keiser, Ber. 1887, 20, 2323).

In presence of water and of oxygen, palladium hydrogen seems to behave as an oxidising agent, this being probably due to the formation of hydrogen peroxide, which in the presence of palladium, behaves as the oxidiser (Traube, Ber. 1889, 22, 1496; Hoppe-Seyler, *ibid.* 2215).

The salts of palladium have so far been but little applied to technical use, but some of them, like potassium palladium chloride, are employed for toning in photography (J. Soc. Chem. Ind. 1911, 1410). The metal is commonly included in the sub-group which includes the metals rhodium and ruthenium. All three are lighter, melt more readily and are more easily volatilised, oxidised, and dissolved than the other metals of the platinum group. The division of the platinum metals into two groups is, however, somewhat arbitrary, and depends mainly on difference in density; and palladium, like osmium, would almost require to be placed alone except as regards this one point, if subdivision were permissible.

#### PALLADIUM COMPOUNDS.

*Oxides.* Palladium monoxide PdO may be prepared as an amber-coloured mass, yielding a black powder, by heating a mixture of a palladium salt with potassium carbonate; or as a bluish-green mass by heating the spongy metal in a current of oxygen at 700°–840°. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by hydrogen or hydrogen peroxide. When freshly precipitated in the cold from a palladous salt with sodium carbonate, the hydroxide is dark brown, and is readily soluble in alkalis. If dried or precipitated from a boiling solution it becomes insoluble. The palladious salts which correspond to this oxide, are of a green, red, or brown colour, and have an astringent taste.

Palladium dioxide PdO<sub>2</sub> may be obtained in an impure hydrated form, soluble in acid, by the interaction of caustic soda and a palladium chloride, or in a purer form, by the anodic oxidation of the nitrate (Wöhler and König, Zeitsch. anorg. Chem. 1905, 46, 323; *ibid.* 1906, 48, 203). It is a vigorous oxidising agent.

Palladium sesquioxide Pd<sub>2</sub>O<sub>3</sub> is best prepared by the electrolytic oxidation of a concentrated solution of palladious nitrate at 8° with a current density of 0.5 cm. amp./cm<sup>2</sup>; but if the electrolysis is prolonged, the dioxide is formed (Wöhler and Martin, *ibid.* 1908, 57, 398). It forms a dark brown unstable powder; gives unstable solutions in hydrochloric acid, and when suspended in ether and mixed with alkali chlorides, on addition of hydrochloric acid, the double chlorides PdCl<sub>2</sub>·2MCl are formed, which in contact with water yield the salts M<sub>2</sub>PdCl<sub>6</sub>.

*Halogen compounds.* Palladium chloride PdCl<sub>2</sub> may be prepared by the action of air or of chlorine and hydrochloric acid on the metal, or by heating palladious sulphide in dry chlorine (Matignon, Compt. rend. 1903, 137, 1051).

It crystallises with 2 mols. of water with a reddish-brown colour; loses water on heating and becomes dark brown, and at a red heat forms the monochloride  $\text{PdCl}$ , a red-brown powder. Palladious chloride, yielding the crystalline compounds  $\text{PdCl}_2 \cdot \text{CO}$ , m.p.  $197^\circ$ ;  $\text{PdCl}_2 \cdot 2\text{CO}$ , m.p.  $142^\circ$ ;  $2\text{PdCl}_2 \cdot 3\text{CO}$ , m.p.  $132^\circ$  (Fink, Compt. rend. 1898, 126, 646).

Palladious chloride forms double chloride with other metals known as *chloropalladites* of the type  $\text{M}_2\text{PdCl}_6$  and Krell, Ber. 1905, 38, 2105; potassium salt is used in (J. Soc. Chem. Ind. 1901, 1, 849).

Many organic basic derivatives of these salts are known (Hardin, J. Amer. Chem. Soc. 1899, 21, 943; Rosenheim and Maass, Zeitsch. anorg. Chem. 1898, 18, 331; Gutbier, Ber. 1905, 38, 2105; Gutbier and Krell, *ibid.* 3869; *ibid.* 1906, 39, 616, 1292; Gutbier and Woernle, *ibid.* 2716).

Palladic chloride is not known in the free state, but only as double salts of the type  $\text{M}_2\text{PdCl}_6$ , and in combination with tertiary cyclic organic bases, and with tertiary bases, as intensely coloured products (Mohlan, Ber. 1906, 39, 861; Gutbier and Woernle, *ibid.* 4134).

The sesquichloride  $\text{PdCl}_3$  is obtained as above, and in the form of double salts  $\text{M}_2\text{PdCl}_5$  (Wöhler and Martin, *l.c.*). Bromides and iodides of palladium are also known (Gutbier and Krell, *l.c.*; Smith and Wallace, Zeitsch. anorg. Chem. 6, 380).

**Ammonia salts.** Ammonia acts on palladious salts forming *palladosammine* and *palladiodiammine* compounds, analogous to the corresponding platinum compounds (Müller, Annalen, 1853, 86, 341). Palladium derivatives of hydroxylamine (Zeisel and Nowack, Annalen, 1907, 351, 439) and of hydrazine chloride (Burdakoff, J. Russ. Phys. Chem. Soc. 1909, 41, 757) have been prepared.

When a 33 p.c. solution of a primary alkyl amine is added slowly to an excess of palladious chloride or bromide solution, rose-red needles of a salt  $\text{Pd}(\text{NH}_3)_4\text{X}_2$  are thrown down. On heating to  $200^\circ$ , the salt decomposes into palladosammine  $\text{PdR}_2\text{X}_2$  ( $\text{R} = \text{mol. of amin.}$ ) and a volatile solution, (c) by solution and precipitation with the desired halogen hydride.

The palladosammine chlorides are of a pale-yellow colour, the bromides dark-yellow, and the iodides brownish-yellow. They all yield colourless solutions in concentrated ammonium hydroxide (Gutbier and Krell, Ber. 1906, 39, 1292; Zeitsch. anorg. Chem. 1905, 47, 23). Certain diamines also yield rose- or flesh-coloured salts with palladous halides of the composition  $\text{PdD}_2\text{X}_2 \cdot \text{PdX}_2$  ( $\text{X} = \text{halogen}$ ,  $\text{D} = \text{diamine}$ ) (Gutbier and Woernle, Ber. *l.c.*; see also Rosenheim and Maass, *l.c.*).

**Palladious nitrate**  $\text{Pd}(\text{NO}_3)_2$  is formed by dissolving palladious chloride in nitric acid. It crystallises in prisms, which on addition of water are converted into a brown powder of composition  $\text{Pd}(\text{NO}_3)_2 \cdot 3\text{Pd}(\text{OH})_2$ .

**Potassium palladionitrite**  $\text{Pd}(\text{NO})_2 \cdot \text{K}_2$  is a pale-yellow crystalline powder formed by adding

potassium nitrite to a hot solution of potassium palladichloride, and according to Pozzi-Escot and Couquet (Compt. rend. 1900, 130, 1073), this may serve as a micro-chemical test for palladium.

**Palladious cyanide** is a pale-yellow salt obtained by the action of mercuric cyanide on a palladious salt.

**Palladious thiocyanates** are described by Belucci (Atti. R. Accad. Lincei. 1904, v. 13, ii. 386).

**Palladious sulphate**  $\text{PdSO}_4 \cdot \text{H}_2\text{O}$ , formed by the solution of the hydroxide in sulphuric acid, forms olive-green crystals which are decomposed by water forming a basic salt  $\text{Pd}(\text{SO}_4)_4 \cdot 7\text{Pd}(\text{OH})_2$ .

The *sulphides*  $\text{Pd}_2\text{S}$ ,  $\text{PdS}$ , and  $\text{PdS}_2$ ; *selenides* (Roessler, Zeitsch. anorg. Chem. 1895, 9, 31; see Petrenko-Kritchenko, *ibid.* 1893, 4, 247), and also *thiosulphates* are known (see, too, Hofmann and Höchtle, Ber. 1904, 37, 245).

**Palladium silicides** are formed when the elements are heated together to  $500^\circ$ – $600^\circ$  (Lebeau and Jolibois, Compt. rend. 1908, 146, 1028).

A number of complex nitrites, sulphites, phosphates, and oxalates have been prepared (Loiseleur, Compt. rend. 1900, 131, 262; Vézès, Bull. Soc. chim. 1899, [iii.] 21, 172; Rosenheim and Itzig, Zeitsch. anorg. Chem. 1900, 23, 28).

For certain other organic compounds of palladium, see Hofmann and Rabe, *ibid.* 1897, 14, 293; Kurnakoff and Swodareff, *ibid.* 1899, 22, 384. Z. K.

**PALMITIC ACID**  $\text{CH}_3[\text{CH}_2]_{14}\text{COOH}$  is a constituent of the greater number of animal and vegetable fats, in which it occurs as the glyceride *tripalmitin*  $\text{C}_3\text{H}_5(\text{C}_{16}\text{H}_{31}\text{O}_2)_3$ . It is obtained from palm-oil (whence its name) by saponification; also by treating oleic acid with caustic alkali. It also occurs in Chinese wax (from *Sapium sebiferum* [Roxb.]), in Japanese wax (from *Rhus cetti*, human *sebum*); Maskelyne, J. 1855, 519; Brodie, Annalen, 71, 159; Krafft, Ber. 1888, 2265; Varrentrapp, Annalen, 35, 210). Crystallises from alcohol in needles; m.p.  $62^\circ$ , and distils, with slight decomposition, between  $339^\circ$  and  $356^\circ$ , b.p.  $268.5^\circ$  (100 mm.); sp.-gr. 0.8527 at  $62^\circ/4^\circ$ .

*Cetyl palmitate*  $\text{C}_{16}\text{H}_{31}\text{O}_2\text{C}_{16}\text{H}_{33}$  is the chief constituent of spermaceti (Heintz, Annalen, 80, 297). Crystallises from ether in thin plates; m.p.  $53.5^\circ$ .

*Ceryl palmitate*  $\text{C}_{16}\text{H}_{31}\text{O}_2\text{C}_{17}\text{H}_{35}$  is the main constituent of opium wax (Hesse, Ber. 1870, 639); m.p.  $79^\circ$ . *Myricyl palmitate*  $\text{C}_{16}\text{H}_{31}\text{O}_2\text{C}_{18}\text{H}_{37}$

is found in beeswax (Brodie, Annalen, 71, 159); m.p.  $72^\circ$ .

By heating palmitic acid with glycerol, the mono-, di-, and tri- esters are prepared. *Tri-palmitin* melts at  $66^\circ$  (see also Smith, Amer. Chem. J. 6, 230; Stenhouse, Annalen, 36, 54).

For estimation and other details, v. OILS, FIXED, AND FATS.

**PALMITIN** v. OIL, FIXED, AND FATS.

**PALM KERNEL OIL.** Palm kernel oil is obtained from the kernels of the palm tree fruit. The kernels are collected by the natives after the palm oil has been recovered from the fleshy

part of the fruit; the shells are removed by cracking each nut separately with a stone or hammer. This work is chiefly done by women and children. Owing to the laboriousness of this process, and also to the fact that no more than about 15 pounds of kernels are obtained by one worker in a day, and that the kernels have to be carried to the market, enormous quantities of palm nuts are wasted. Although recently several nut-cracking machines have been sent to the west coast of Africa, they have hitherto not been able to supplant manual labour. The kernels are collected at the coast stations and shipped to Europe. The chief receiving ports are Hamburg, Liverpool, and Marseilles.

In Europe the kernels are screened to free them from shells, stones, nails, hammerheads, then passed over magnetic separators, and finally ground between rollers to a paste. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the first process the meal must be pressed twice, on account of the large proportion of fat the kernels contain.

On a commercial scale, the first expression of palm kernel meal is carried out at a temperature of 45°-50°, the second at 55°-60°. Thus 43-45 p.c. of palm kernel oil is recovered.

The press cake contains 6-8 p.c. of oil; its proportion of nitrogen is small (about 2.5 p.c.), hence its value as cattle food is somewhat low. For the same reason the extracted meal has a low manurial value.

The colour of palm kernel oil is white to pale yellow. In the fresh state the oil is neutral and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids.

For physical and chemical characteristics, v. tables under OILS, FIXED, AND FATS.

The chief constituent of palm kernel oil is lauric acid. In addition, there are present smaller quantities of caprylic, capric, caproic, myristic, palmitic, and oleic acids.

Palm kernel oil is largely used for soap-making. The freshest oil is employed in the manufacture of vegetable butter (like 'cocoa nut oil') and of 'chocolate fat.' In this latter manufacture a hard fat ('palm nut stearine') is obtained; the liquid 'palm nut oleine,' being a by-product, is used in soap-making.

J. L.

**PALM OIL.** Palm oil is obtained from the fleshy part of the ripe fruit of the palm tree *Elaeis guineensis* (Jacq.), which forms vast forests along the west coast of Africa, extending between Gambia and St. Paul de Loanda. The west coast of Africa is practically the only supplier of palm oil. *Elaeis guineensis* forms a very large number of sub-species for the description of which the reader may be referred to "Le Palmier a l'Huile" by Jean Adam (Challamel, Paris).

The favourite habitat of the palm tree is the open country or bushland; it grows frequently where the natives have cleared the virgin forest. The tree is characteristic of the coast line and the lower reaches of the rivers. It will grow in all soils, but does not bear well at a higher elevation than 3000 feet. Under favourable conditions the tree forms a trunk

when five years old, and then begins to bear fruit. The yield afterwards increases and the tree gives its full harvest in its 12th year. This rate of yield is continued throughout the life of the palm tree, which lasts 50-60 years.

Owing to climatic conditions, the process of extraction has been hitherto practised exclusively by the natives, and is an exceedingly crude one. When the fruits ripen, the men climb up the trees and cut off the bunches with 'matchets.' Owing to the height from which the bunches fall, a large quantity of the fruit is bruised, which naturally leads to rapid fermentation and to hydrolysis of the oil. The women and children pick the fruit from the bunches and throw it into a hole dug in the ground and lined with leaves. The flesh of the fruit is at this time hard, and before the kernels can be separated, the flesh must be softened. This is done by sprinkling water on the fruit, covering it over with more leaves, weighted by stones and left for two weeks. During this time the flesh softens, which causes the fleshy part of the fruit to become soft, so that the kernel-palm nut—can be removed more readily. This is done by men, who place the fermented fruits in a mortar, roughly made by lining a hole made in the ground with large flat stones. The fruit is then beaten with long wooden pestles, or the pulp is pressed by hand. The beaten pulp, together with the nuts, is taken out by women and children and placed over another hole, the sides of which have been cemented by plastering with a mixture of palm oil and wood ashes. The pulpy mass is then allowed to rest for a week. During this time, the oil drains into the cemented hole, from which it is ladled out into large calabashes of a size to make up one load.

The oil so prepared represents a superior kind of product. Women and children then pick out the nuts from the pulp, mix the pulp with water and place it in large iron cauldrons, where the whole mass is well boiled and stirred until the oil rises to the top. The oil is skimmed off, and, in some regions, mixed with the first extracted oil or put into separate vessels for the market. Finally, the residue is placed in a bag and squeezed over a hole so as to force out the liquid, from which more oil rises to the top. This oil contains a large quantity of water, and is again boiled out, skimmed off, and placed in calabashes.

The oil is then collected by women—to the nearest coast station, where traders collect it in large barrels, and take it down to the coast station. There the oil frequently undergoes a rough purification by being boiled up with water, and then it is poured through sieves into a ship for shipment. During the last year, efforts were made to introduce European methods of manufacture in the coast stations as well as in the bush in the French, English, German, and Congo territories at the west coast of Africa.

Palm oil has a somewhat sweetish taste; in its perfectly fresh state it is used as a culinary fat in the villages of the west coast of Africa. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at elevated temperatures, and persists even after the oil has been made into

soap. In consequence of the very crude mode of producing palm oil, causing it to remain for a considerable time in contact with fermentable vegetable tissue, hydrolysis rapidly sets in, so that the oil on reaching the coast contains already a notable amount of free fatty acids. Palm oil when shipped from the coast has at least 10-12 p.c. of free fatty acids. The process of hydrolysis, once begun, continues in the barrels during the voyage, and in consequence, commercial palm oils, on arriving at their destination, contain frequently from 20-50 p.c., and even more, of free fatty acids. In such palm oils, free glycerol is found. In old samples the hydrolysis may even reach completion, so that such palm oil practically consists of free fatty acids (Lewkowitsch). The progress of hydrolysis can be observed even in oils kept in glass bottles.}}

The value of a palm oil in the market depends on the care with which it has been prepared, as also on the particular locality from which it is derived. The 'soft' oils are those containing a small quantity of free fatty acids, whereas the 'hard' oils contain a large proportion. The best 'soft' oils come from Lagos and Dahomey. Next in quality are the river oils ('medium' oils); whilst the lowest quality, the hardest oil, is represented by Congo oil.

The colouring matter of palm oil is not affected in the process of saponification. The action of caustic alkalis or linoleic acid in the saponification process it is destroyed. It is also slowly destroyed by exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

The bleaching process most in vogue, and that giving the best results, is the dichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1-3 p.c. of potassium dichromate and the requisite amount of sulphuric acid. The dark 'chrome' liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium compounds and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty-coloured red oils, such as Congo oil, have hitherto withstood all attempts to bleach them.

The chief constituents of palm oil are palmitin and olein. The proportion of stearin hardly exceeds 1 p.c. For the chemical and physical characteristics of palm oil, v. tables under OILS, FIXED, AND FATS.

Palm oil is chiefly used in the soap and candle industries. In the latter industry it is valued *ceteris paribus* by its 'titer.' Being a non-drying oil, it is also employed in the tinplate industry, to preserve the surface of the heated iron sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry, 'palm oil greases' are sold, consisting of palm oil adulterated with cotton seed oil and mineral oil of the sp.gr. 0.905.

J. L.  
PALM RESIN or CEROXYLIN v. RESINS.

PALM SUGAR or DATE-TREE SUGAR. The liquid extract of certain palms is more or

less rich in saccharine substances which are easily obtained. A method of obtaining it has existed in

India from time immemorial, and was found to prevail among the aborigines of America on the discovery of that continent.

The palms which supply sugar are *Borassus flabellifer* (Linn.), *Phoenix sylvestris* (Roxb.), *Caryota urens* (Linn.), *Arenga saccharifera* (Labill.), &c.

Palm sugar is hygroscopic, and appears to be purgative if freely used. To divest it of this property it requires to be refined. The juice is sometimes obtained by cutting off the lower leaves of the crown about the end of October, and stripping the trunk of such as grow upon it to the place where incision is to be made. A bamboo cane is placed at the orifice each evening, by means of which the sap is conducted into vessels which are removed early next morning. In the case of *Phoenix sylvestris*, the tapping is done by making an incision in the wood at the base of the lowest green leaves, and subsequently removing slices of wood until the flow ceases. The cut axis of the inflorescence of *Caryota urens*, and the cut flower axes and cut sheathing spathes of *Borassus flabellifer* yield the sugary juice. The process of extracting the sugar from the sap must be preceded with without delay, as fermentation sets in rapidly, when it is impossible to procure by boiling the syrup or *goor*, i.e. the mixture of molasses and crystallised sugar from which the sugar is extracted. The amount of sugar produced is about 40 p.c. of the syrup.

PALM TREE WAX v. WAXES.

PALYGORSKITE v. ASBESTOS.

PANCLASTITE v. EXPLOSIVES.

PANDERMITE. A natural calcium borate employed in the manufacture of enamels instead of borax, v. COLEMANITE.

PAPAIN or PAPAYOTIN. A vegetable digestive ferment obtained from the unripe fruit of *Carica Papaya* (Linn.), or papaw tree, and used as an alternate to pepsin, from which it differs by being active in neutral and alkaline conditions (v. E. J. Easter, Pharm. J. 1885, 45). The half-ripe fruit when scratched exudes a large quantity of a milky juice, which when dry forms a powder somewhat resembling gum arabic. The name 'papain' is usually restricted to the pure ferment associated with a proteid substance, and is obtained by precipitation with alcohol and separation of albuminous matter by basic lead acetate. The fruit of the papaw tree has long been used in the West Indies to render beef tender. The unripe fruit is split open and rubbed over the surface of the meat previous to cooking. Its action probably depends upon the fact that papain has a digestive action, not only upon muscular fibre, but also upon connective tissue. It digests fibrin and albumin in neutral and slightly alkaline solutions. When injected into the circulation in large doses it paralyzes the heart. It is used to favour the absorption of the blood (T. L. ... &c., 927).

PAPAVERINE v. VEGETO-ALKALOIDS.

PAPAVEROSINE v. VEGETO-ALKALOIDS.

PAPER. The art of modern paper-making consists in uniting or 'felting' together any

fibrous vegetable matter, so as to form a continuous sheet. Owing to the abolition of the paper duties, in 1827, and the consequent rapid growth of cheap literature, the old dictionary definition of paper as 'a substance made of linen or cotton rags' no longer holds good. As a matter of fact, these substances constitute but a small fraction of the raw materials of the paper-maker.

Any vegetable substance possessing a sufficiently fibrous structure can be utilised. Occasionally both animal and mineral fibrous substances—such as wool, silk, or asbestos—are employed, either alone or as admixtures.

In order to give some idea of the variety of materials from which paper can be or has been manufactured, we may cite a book that was published at Regensburg, Germany, by Jacob Schaeffer in 1765, the paper of which was made from about sixty different sources, amongst which the following are curious and interesting: sawdust, hop-vines, hornets' nests, peat, moss, various woods,

majority of cases the paper is of very inferior quality, the pulp being coarse and unbleached. A similar book is that containing the poems of the Marquis de Villette, published in 1786. Another, of historical interest, is one the paper of which was made entirely from straw. It was published in England in 1800.

Notwithstanding the variety of materials available, rags of various kinds continued to form the chief raw material of the paper-maker until the year 1860, when Mr. Thomas Routledge introduced esparto grass (*v. ESPARTO*). This material, which possesses many advantages, is very extensively used in this country. Of late years, however, owing to the enormous increase in the demand for paper, it has been largely supplemented by straw, and more especially by wood.

The chemical characteristics of the paper-makers' raw materials have already been discussed in the article *Cellulose*. These materials consist, with the exception of cotton and linen rags, of one or other, or a mixture, of the various compound celluloses; and the treatment they undergo consists essentially in isolating the cellulose by chemical means. This treatment is accompanied by separation, more or less complete, into individual cells, which vary in length from about 1.5 mm. in the case of esparto to 30 mm. in the case of flax. This chemical splitting up into cells is supplemented by a mechanical operation known as 'beating,' whereby the material is still further reduced (*v. infra*).

The various processes that the different forms of cellulose undergo before being made into paper may be divided into four main branches—(1) cleaning, (2) boiling, (3) bleaching, (4) beating, or reducing to pulp. In addition to these, there are the processes of sizing, colouring, &c., which will be included in No. 4.

**1. Cleaning.** This is a purely mechanical process, and consists in removing from the raw material adventitious matter, such as sand, dirt, &c. Part of this work is done by hand-labour, especially in the case of rags, but the modern tendency is to replace hand-labour as much as possible by machinery. In the case of rags cut by machinery, the pieces, spread on to a table

made of coarse wire gauze, are examined by girls, and such articles as buttons carefully removed. At the same time the rags are sorted into various kinds, such as cotton, linen, jute, canvas, &c., each kind being separately stored in boxes. This process, which is somewhat costly, is only practised in the case of rags intended to be used for high-class paper. The usual plan, which may also supplement the hand-labour, is to pass the cut rags through a 'willow.' This consists of two wrought-iron drums, furnished with teeth, which, when the drums revolve, pass rapidly near stationary teeth fixed in the frame in which the drums work. The sides and top are covered in with iron doors, and underneath is a grating for the escape of dust. The rags are fed into the drums by an endless travelling platform, and pass from thence into a duster, consisting of a kind of hollow cylinder made of iron bars covered with wire cloth. The cylinder revolves almost horizontally, a slight dip being given to it in order that the rags may be carried forward to the lower end. The 'willows' used for esparto and various other fibres are similar in principle. The cleaned and dusted rags, or other material, are carried forward by an endless felt to the boilers, where the next operation is performed.

**2. Boiling.** The boiling processes vary considerably with the kind of material. We will discuss them in the order of their simplicity.

(a) *Rag boiling.* Rags, being for the most part refuse from textiles made from pure or nearly pure cellulose, require a comparatively light treatment. It may be conducted either in spherical or cylindrical boilers, or in the 'vomiting' boilers, described under *Esparto*. In the case of spherical boilers the heating is caused by 'live' steam: cylindrical boilers are usually jacketed. It is preferable to cause the boilers to revolve. They are furnished with inlet and outlet steam-pipes, pipes for running in liquor and water, man-holes for filling and emptying, and safety valves, pressure gauges, &c. The alkali used may be either caustic soda, caustic

or a mixture of the latter. The proportion of alkali depends mainly on the state of the rags and the nature of the substances to be removed, and also to some extent on the pressure of steam employed and the duration of the operation. As a general rule applicable to rags and all other fibres, it may be stated that the higher the pressure and the longer the time occupied, the less alkali (within, of course, certain limits) is necessary. The amount of alkali varies from 1 p.c. of 70 p.c. caustic soda in the case of the higher qualities of rags to 5 p.c. in the case of lower qualities.

The pressure also varies considerably—say, from 5 to 60 lbs. per square inch. In the opinion of some the lower pressures are to be preferred, as at the high temperature associated with higher pressure there is a tendency to fix a certain amount of dirt and colouring matter in the rags, thereby defeating to some extent the object of the boiling. After boiling, the rags may be washed in the boiler or in a separate washing engine which will be subsequently described.

An effective method of cleaning in exposing the rags, continuously wetted with caustic soda solution, to an atmosphere of steam at 10 lbs. pressure. The dry and dusted rags are



packed into waggons, fitted with perforated bottoms. The waggons are then run into a horizontal cylindrical vessel, called a 'kier,' which they almost completely fill. When in position, a pipe at the bottom of each wagon fits tightly over a pipe passing through the bottom of the kier and connected by means of a centrifugal pump with an outside pipe communicating with the top of the kier. Caustic soda solution is run in, and is made to circulate through the rags by means of the pump. One end of the kier is closed and the other is fitted with a V-shaped door, which falls into a slot of similar shape, making a readily-adjusted steam-tight joint. The door is raised and lowered by hydraulic pressure. The apparatus is known as the 'Mather Steamer Kier.'

(b) *Esparto boiling.* Esparto, being a compound cellulose, requires a more drastic treatment than rags. The first process that esparto undergoes is that of 'picking.' This operation, which is done by hand, consists in removing root-ends, weeds, &c. It has latterly been largely dispensed with, and a more complete mechanical treatment substituted. For this purpose the grass is passed through a willow and duster similar in principle to that described under the head of Rags.

After passing through the machine the grass is in some cases carried along a travelling belt, and is discharged direct into the boiler. These are almost invariably stationary, as a revolving boiler is apt to cause the grass to form into dense masses, which resist the action of the soda used in boiling. An esparto boiler is shown in Fig. 1. It is furnished with a perforated

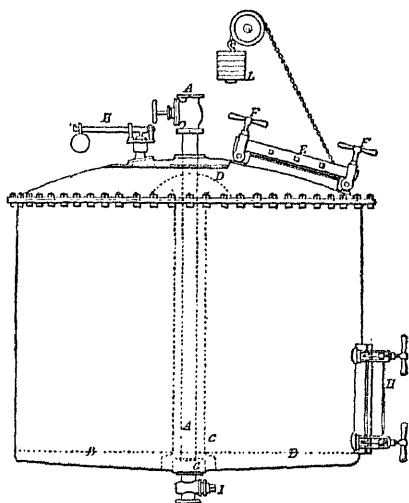


FIG. 1.

false bottom B, on which the grass rests. Steam enters by the pipe A, which reaches below the false bottom and causes the liquor to rise up the outer pipe C, strike against the 'bonnet' D, and distribute itself over the grass in a fine spray. The door E is for filling in the grass, and the door H for emptying. The boiler is fitted with a safety valve K. Each boiler holds about 60 cwt. of grass, and the operation lasts about five

hours. The amount of soda varies according to the nature of the esparto, Spanish requiring less than African: about 16 lbs. of 70 p.c. caustic per cwt. is an average quantity. The steam pressure also varies from 5 lbs. to 45 lbs. per square inch. Occasionally an open boil is used. The modern tendency is to employ the higher pressures, as being more economical of time and soda. Other forms of vomiting boilers have lately been introduced, in which the vomiting arrangements are fixed either outside the boiler altogether, as in Roeckner's, or are placed at the sides, as in Sinclair's, thus giving more space for the grass. The alkali used is invariably soda. The boiling operation being completed, the liquor is run off from a cock at the bottom of the boiler, and the grass partially washed with water in the boiler. This also has the effect of cooling the grass and enabling the workmen to remove it to the washing engine or 'breaker.'

In some mills the grass is placed in a series of tanks similar to those used for dissolving black ash, where the washing can be effected with a very small quantity of water—a very important matter from the point of view of recovery of the soda.

The washing engine, which may be used for any other fibres besides esparto, is shown in Fig. 2. It consists of a rectangular vessel with rounded ends, in the centre of which is the mid-feather B. The action of the roll A, which is fitted with clusters of steel knives G, disintegrates the grass and causes it to circulate round the engine. The floor is sloped as shown by the dotted lines P and P', the effect being to cause the grass to pass under the roll A, the knives of which pass close to similar plates I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z, fixed to the 'bed-plate' I. The pressure between the roll and the 'bed-plate' can be varied at will by means of the wheel M.

A continuous stream of water is run into the engine, and the dirty water is lifted by means of the 'drum washer' C, the periphery of which is covered with fine wire gauze. The centre of the drum is formed of a conical tube, the narrow end of which is towards the 'mid-feather.' The dirty water passing through the wire gauze is lifted by the drum C, and is discharged into the centre of the drum, and is then carried down the 'mid-feather,' which is made hollow for the purpose.

The grass having been thoroughly washed and reduced to the state of pulp by means of the steel knives in the roll, is ready for bleaching. This operation will be described hereafter.

(c) *Straw boiling.* Straw esparto in its chemical characteristics, but being more highly lignified a somewhat severer treatment is required. This is obtained either by boiling at a very high pressure, 60-80 lbs., or by using a larger proportion of caustic soda (18-20 lbs. per cwt.). In treating straw for use in high-class papers, it is customary to blow it through a large receptacle, the floor of which is covered by a sieve kept in vibratory motion. The receptacle is arranged that heavy particles, such as sand or stone, fall through the grid in the first section, while the heavier particles of straw, such as the knots, are carried forward to the second section. The very light pieces are carried through to the third section.

The advantages of this system of treatment are, that the subsequent operations can be conducted with greater uniformity. The boiling operation usually takes place in large revolving boilers. Owing to the rotary action of the boiler, the straw is in the state of fine pulp and readily flows through a 3-inch pipe. It is run into tanks, the bottoms of which are formed of perforated tiles. The liquor is run off and fresh water added until all soluble matters have been removed. It is then ready for bleaching.

In making straw pulp of fine quality it is sometimes found advantageous to pass the washed pulp between horizontal rollers, whereby the knots and any are finely ground and rendered more easily bleached.

(d) *Wood v. CELLULOSE.*

(e) *Other fibres.* There are a number of fibrous materials which are available for the paper-maker, such as jute, manilla, adansonia, &c., the treatment of which calls for no special

notice. The nature of the treatment which they undergo varies with the kind of paper for which they are intended. The greater number of such fibrous materials are used for papers where strength is of far greater importance than colour or appearance, such, for example, as brown papers and packing papers. In such cases the paper-makers aim at a minimum resolution of the fibre, so as to preserve the strength and increase the yield. In the case of jute the individual fibres are very short and weak, and a strong and perfectly white paper made from jute is an impossibility. If, however, the filaments are not completely resolved, a strong fibre can be obtained.

The cheapest method of treating such fibres is to boil them under pressure in a solution of lime. This treatment is not nearly so effective as that with caustic soda, and the fibre produced is coarse and hard. The yield is, however, high.

There is another very important material

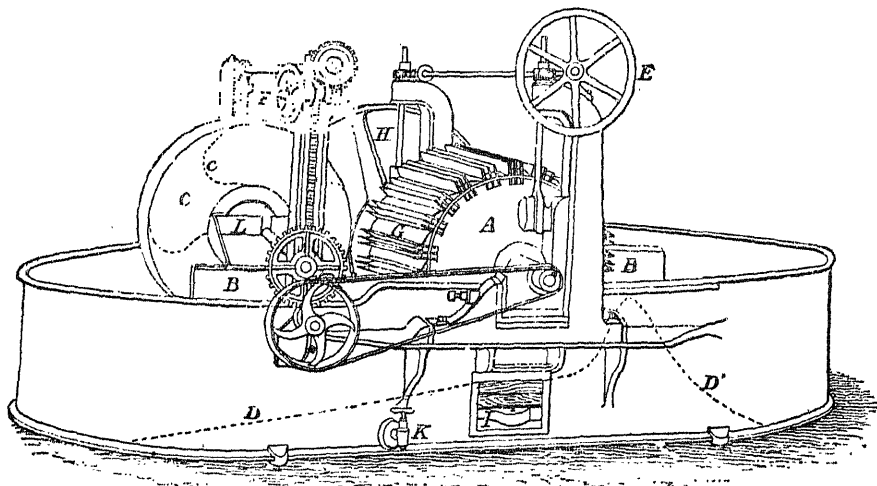


FIG. 2.

which may be mentioned here, viz., mechanical wood-pulp. A large quantity of this is used in the cheaper kinds of paper. It is prepared by disintegrating wood by mechanical means alone. Blocks of wood, from which the knots have been removed, are placed in a large tank, and at the same time the stones. The wood is so placed that the fibres are torn off in the direction of their length in order to secure as great length as possible. The stream of water carries the pulp forward as fast as it is made. The larger undisintegrated portions are removed by screens of coarse wire cloth. In order to still further refine the pulp it is caused to pass between two horizontal cylinders of sandstone, the upper one of which revolves rapidly.

Where power is cheap such pulp can be economically prepared; but, however, at best but a poor substitute for the other pulps. Paper made with it has but little strength, and is very susceptible to atmospheric action. The woods chiefly used are white pine and aspen;

the latter yields a pulp of good colour but little strength.

**3. Bleaching.** The processes of bleaching paper-pulp are practically identical for all classes of material. The agent employed is a solution of calcium hypochlorite, made by dissolving bleaching-powder in water. The operation may be conducted in the breaking engine previously described, or in a separate engine called a 'potcher,' which is similar in construction, but the roll is furnished only with blunt blades, which serve as paddles to cause the pulp to circulate. Sometimes large potchers made of brick and cement are used.

A system that is being very largely used, is that known as the 'Continuous Bleaching Process,' where the bleaching is done in a series of towers (v. Fig. 3). The pulp, after washing and breaking, is pumped into the first tower, and after partial removal of the water by means of a concentrator, is bleached while being kept in circulation by means of a centrifugal pump placed at the base of the tower. If only one tower is in

use, the stuff can be pumped up continuously to the top of the tower, where it is distributed by means of a cone towards the sides. Where there is a series or 'battery' the pulp is pumped up into the next tower, and so on through the series. It is usual to have a second concentrator fitted to the last tower for the purpose of removing the spent bleach, and the soluble non-cellulose constituents.

The advantages claimed for this system are (1) comparatively little power is required for (2) an approximate saving of 25 p.c. owing to the concentration of the pulp under which the bleaching process is carried out, (3) the bleaching is carried out at the ordinary temperature, thus obviating any possibility of rendering the pulp.

The action of the calcium hypochlorite may be hastened by heat, the 'potchers' being provided with steam pipes for this purpose, or by the addition of sulphuric or hydrochloric acids. The best results are obtained by the action of bleaching solution alone, in which case a longer time must be given. This is more than com-

pensated for by the extra yield of pulp and its greater strength.

The amount of bleach necessary to bleach from about 7 p.c. in the case of straw to about 15 p.c. in the case of wood. These amounts are calculated on the unboiled materials.

Chlorine gas as a bleaching agent was formerly used for rags, but is now almost entirely superseded. As a matter of fact, chlorine will not bleach the majority of pulps; it enters into combination with the fibre substances, producing yellow-coloured combination products. Advantage has been taken of this fact by F. C. Glaser in his process for treating straw. The straw is first boiled with a reduced quantity of soda; it is then drained and exposed to the action of chlorine gas. A subsequent treatment with bleaching liquor produces a very pure white pulp.

The bleaching of pulp by means of the products of the electrolysis of chlorides has attracted much attention. Of the various processes introduced, one of the best known is that

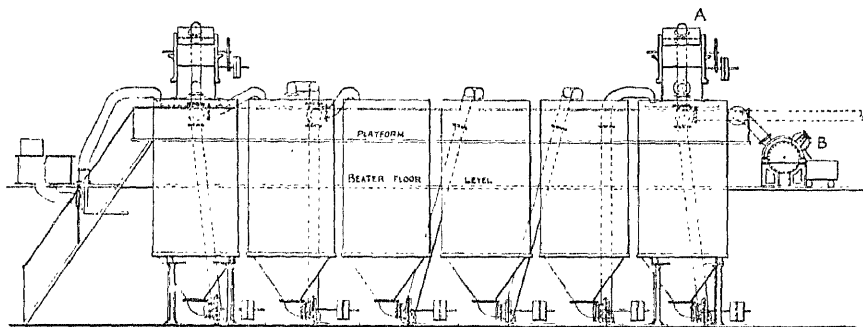


FIG. 3.

of M. Hermite, which is in successful operation in many mills on the Continent. It depends upon the fact that when a solution of magnesium chloride is electrolysed, magnesium hypochlorite is formed, which possesses considerably greater bleaching efficiency than calcium hypochlorite of equal strength.

After bleaching, and before the next operation of beating, the pulp is sometimes purified by passing it over a 'presse-pâte,' which consists of a strainer and that part of a paper machine on which the web of paper is formed. The pulp is thus made into a thick continuous sheet; at the same time all soluble impurities, such as calcium chloride, &c., are removed.

The 'presse-pâte' system has latterly been largely superseded by the use of 'concentrators' such as the 'Couper' concentrator.

This consists of a revolving drum fitted with a central cone arranged so as to deliver water at both ends. The drum is of perforated brass and covered with wire-cloth. The pulp is put in by a butterfly throttle valve into a chamber whereby it is caused to flow along the whole width of the drum cover. The cover or hood is so arranged by means of packing, that the water in the beaten stuff can be forced through the wire-cloth of the revolving drum, at a pressure of 2-3 lbs. to the square inch,

leaving a mat of fibre upon it. The fibre is then picked off the wire by means of a jacketed conch roll, and again removed by means of a wooden doctor, and deposited into boxes.

This action secures a higher concentration of pulp than the 'presse-pâte,' as in the latter case the water is separated from the fibre by gravity only.

**4. Beating.** The bleached pulp, before being made into paper, requires to be beaten up into fragments of from 1-2 mm. in length. In the case of esparto, straw, and wood, this length is that of the individual fibres; the beating of cotton and flax, is confined to comminuting the bundles produced by the boiling and bleaching processes. But in the case of cotton and flax, the individual fibres of which are about 30 mm. in length, a much more extended mechanical treatment is necessary. The operation is conducted in an engine called the 'beating engine,' similar in construction to the breaking or tearing engine described (Fig. 2), the difference being that the roll of flax is replaced by a larger number of knives.

The distance between the roll and the bedplate is arranged so as to 'tear' the fibres, instead of 'cutting' them, so as to give them the maximum amount of felting power. In

some cases the knives are made of bronze in order to avoid contamination of the paper with iron-rust. Various other forms of beating engines have lately been introduced which differ somewhat in the arrangement of the various parts, but which do not call for special notice.

It is in this stage of the treatment of the pulp that the various loading, sizing, and colouring materials are added. Before doing this, however, it is necessary, unless the operation has been previously performed in the washing engine, to remove the excess of bleaching solution. This may be done by simple washing, many beating engines being provided with washing drums for the purpose; or the bleach may be neutralised by the addition of an antichlor, such as sodium sulphite.

**5. Loading.** Most papers, except perhaps the very finest 'writings,' contain some added mineral matter, such as 'pearl hardener' (calcium sulphate, ground or precipitated, for the better qualities, and china clay for the cheaper papers. This addition cannot, unless carried to excess, be considered an adulteration, as it fills up the pores of the paper, and enables it to take a better surface under the calender.

**Sizing.** All writing papers, and most printing papers, require to have some material added to them that will enable them to resist ink. This can be done in two ways—viz., by engine-sizing and tub-sizing: the former is done in the engine itself, the other in the finished paper. Engine-sizing consists in the addition of resinate of aluminium, which is precipitated in the pulp by the mutual decomposition of resinate of sodium, prepared by dissolving rosin (colophony) in sodium carbonate, with a solution of alum or aluminium sulphate. In addition to the resinate of alumina most papers contain starch, which may be dissolved in water and mixed with the resinate of soda, or may be added undissolved: the former is the plan usually adopted. Almost all papers, even blotting papers, contain starch, which is not interfering with the paper, but has little or no sizing property, and therefore does not prevent the paper being absorbent. The amount of alum added to pulp is largely in excess of that necessary to fully precipitate the resin; the excess appears to be necessary in order to get a hard paper. It probably has some action on the cellulose itself. The excess, moreover, tends to brighten the colour of the paper.

**Tub-sizing.** This consists in passing the finished paper, either in the form of sheets or in the web, through a solution of gelatin to which alum has been added. Occasionally soap is added to the gelatin. When alum is added to a solution of soap and gelatin, the soap is decomposed and an infinitely fine precipitate is produced, which forms with the gelatin a kind of emulsion. The addition of the soap enables the paper to take a high surface with a minimum of pressure under the calender.

**6. Colouring.** Most bleached pulps have a slight yellow tinge which requires to be complemented by the addition of blue and pink in order to produce a perfectly white paper. The blues usually employed for this purpose are ultramarine and smalts, and occasionally aniline blues; the pinks are either preparations of cochineal or aniline. For the production of

coloured papers a variety of different colouring matters are employed in addition to those mentioned, such as Prussian blue, chrome yellow, Venetian red, &c.

The addition of the loading, sizing, and colouring materials proceeds at the same time that the pulp is being 'beaten.' When this is completed the pulp is ready to be made into paper.

#### 7. Making into paper (*Hand-made paper*).

This is made on a mould of wire-cloth, furnished with a moveable frame of wood called a 'deckle,' extending some distance above the surface. The workman dips the mould with its 'deckle' into a vat containing the beaten pulp largely diluted with water, and removes more or less pulp, according to the thickness of paper required. He, then, by dexterous lateral movements causes the fibres to unite and form a continuous sheet; at the same time the excess of water drains away. The 'deckle' is then removed, and the wet sheet of paper transferred to a piece of felt. This operation is continued until a number of sheets of paper and pieces of felt have accumulated, forming what is called a "post." They are placed in a press to remove a further quantity of water. The sheets are then passed through a solution of gelatin, and hung up on lines or poles to dry. When dry the sheets are calendered.

Comparatively little paper is now made by hand on account of the great expense of labour; it is, however, preferred for bank-notes, drawing-paper, &c., on account of its uniform strength. Owing to the fact that a shaking motion in every direction can be given to the mould, the fibres are irregularly distributed, and the maximum of felting power is obtained, whereas in machine-made paper, as will be seen in Figs. 4 and 5, the fibres tend to place themselves in parallel lines in which the stream of pulp flows. Such paper, therefore, is strongest across the web.

**Machine-made paper.** The modern Fourdrinier paper machine, so-called from the original inventor, consists essentially of an endless mould of wire-cloth on to which a continuous stream of pulp flows and on which a continuous sheet of paper is formed. On leaving the wire-cloth the wet sheet of paper passes through a series of rollers and over heated cylinders and calenders whereby it is dried and finished. The machine is shown in side elevation Figs. 4 and 5.

The pulp on leaving the beaters flows into a large store vessel called a stuff-chest where it is diluted to the proper consistency with water. It is furnished with agitators to keep the pulp uniformly distributed. From here it is pumped and delivered under a constant head, to the sand tables. These consist of a long series of shallow troughs, the bottoms of which are covered with pieces of felt or thin strips of wood placed across the direction of the stream of pulp and at a slight angle, the object of which is to retain any particles of sand or dirt. The pulp passes from the sand tables to the strainers, which are usually of the revolving type, and like the old flat type of jog strainer or knoter consist of strong bronze plates having a large number of fine V-shaped slits cut in them. The slits are from 2-3 inches long, and vary in width from 0.007 to 0.05 of an inch. These slits allow only the fine fibres to pass, retaining all unboiled or

unbleached portions of fibre or other impurities. The passage of the stream of pulp through the slits is assisted by giving a vigorous shake to the strainer plates or by means of a pump placed below. One of these strainers is shown at *c*; the shake is produced by the cam *a* acting on the hammer *b*.

The strained and purified pulp passes from the strainer on to an endless travelling wire-cloth which is carried by a large number of small rolls *f''* and by the large rolls *f'* and *g*. The amount of pulp flowing, and consequently the thickness of the finished paper, is regulated by the sluice *e*. The thickness also depends upon the rate at which the wire-cloth travels; it may vary from 60 to 600 feet per minute.

Travelling with the wire-cloth are two endless thick india-rubber bands *i* called 'deckle straps.' These can be regulated at any distance from each other and serve to determine the width of the sheet of paper. The rolls *f''* and the wire-cloth are carried by standards *g''* which are jointed at their lower ends. At the top they are connected with a rod having a rapid to-and-fro motion which is communicated to the wire-cloth. This shaking motion serves to some extent to neutralise the tendency of the fibres to set themselves in the direction of the flow of the pulp.

The small rolls *f''* cause the excess of water to pass more freely through the wire-cloth. As the sheet of paper passes along, it goes over the vacuum boxes *l* which are connected with air-pumps, by which a further quantity of water is removed from the sheet of paper.

Underneath the wire-cloth is a box *k* called a 'save-all.' The water passing into it holds in suspension a certain amount of fibre. This fibre can be recovered by passing the water through a filter or the water may be used to dilute a fresh quantity of pulp. Any pattern, or 'water-mark' as it is called, may be produced on the paper by causing a light skeleton roll, called a 'dandy roll' covered with raised wire in the form of the . . . . . to press lightly on the wet paper . . . . . placed between the vacuum boxes *l*. After passing the last box *l* the still wet paper passes between the 'couch-rolls' *ac*. These are covered with felt and serve by their pressure to still further dry the paper. The paper here leaves the wire-cloth and is transferred to an endless felt which travels in the direction of the arrows over the roll *k*. On its journey, it passes between the 'first-press rolls' *x*, and then through the 'second-press rolls' *z*. The paper, being still weak, is supported by a felt travelling on the rolls *z*. After leaving the 'second-press rolls' *z*, the paper is carried to the drying cylinders *m*, heated with steam, of which there may be as many as twelve or more.

They are generally divided into two sets, between the sets being a pair of highly polished heated rollers *n* called 'smoothers.' After leaving the last drying cylinder the paper passes through the calender *o* and is then wound off at *p*.

*Single cylinder machine.* In the single-cylinder or 'Yankee' machine, the paper after having been formed on a wire cloth in substantially the same manner as in the Fourdrinier

machine, is dried by passing over one very large cylinder.

In another form of machine the paper is formed on the periphery of a cylinder covered with wire cloth, which revolves in a vessel containing the pulp.

**Calendering.** It is sometimes necessary to give a greater 'surface' to a paper than is acquired by the calender at the end of the machine. This may be done in several ways. One method, called 'web-glazing,' is to pass the web of paper between alternate rolls of polished iron and highly compressed cotton or paper. Another method called 'plate-glazing,' consists in passing a bundle of sheets of paper alternated with polished zinc or copper plates, between a pair of rolls to which great pressure is applied.

Still another method, which is known as 'friction-glazing,' is to pass the web of paper between two rolls, one of which travels at a much higher rate than the other. After calendering, the paper only requires cutting and sorting before being placed on the market.

**Soda recovery.** Formerly, before the introduction of the Rivers Pollution Act of 1876, all liquors in which esparto and other fibres had been boiled were thrown away; it is now the practice to recover the soda contained in them by evaporating to dryness and incinerating the residue, thus obtaining the soda in the form of carbonate. This has in most cases been found to be highly remunerative. Various forms of apparatus for economically evaporating large quantities of water have from time to time been introduced. These can be divided into two types, (1) the direct evaporating plants under

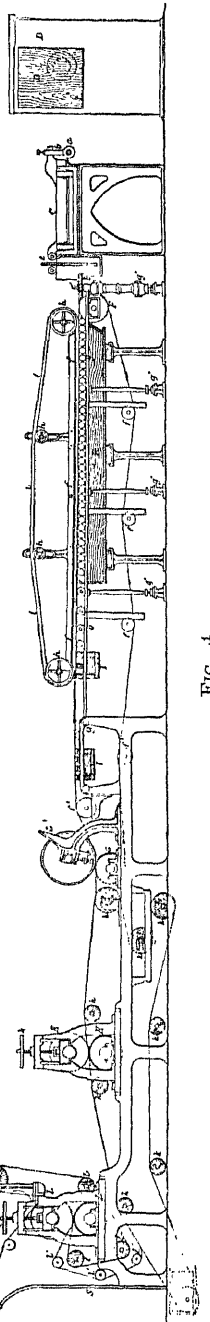


Fig. 4.

ordinary atmospheric pressure, and (2) single or multiple effects, where evaporation is carried on under a partial vacuum. A very effective form representing the first type is that known as the Porion evaporator, which consists of a

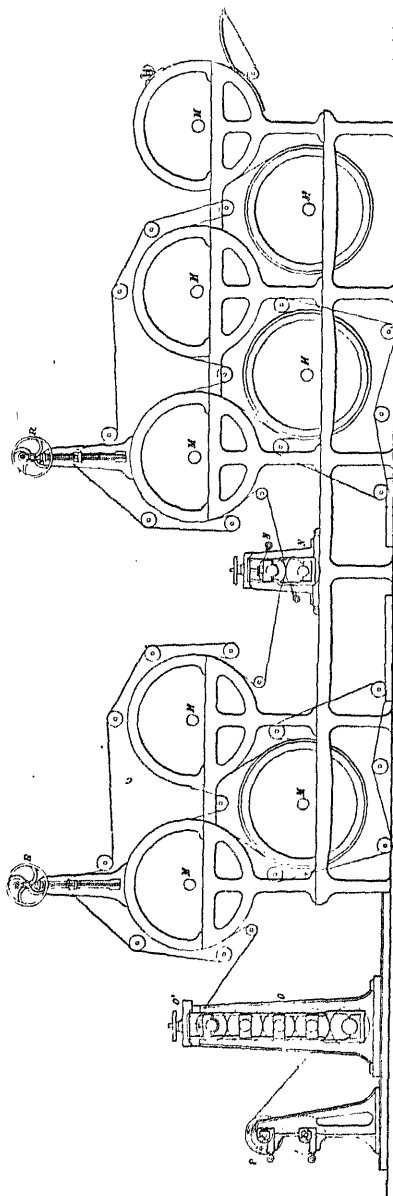


FIG. 5.

large brick chamber on the floor of which the liquor is placed. A number of rapidly revolving fanners stir up the liquor and distribute it in the form of a very fine spray. The chamber is connected with a reverberatory furnace where the evaporated product is incinerated, the waste heat from which serves for

the preliminary evaporation. This evaporator, working with a partial vacuum, is capable of producing 1 ton of soda ash for an expenditure of about 27 cwt. of coal.

There are several forms representing the second type, one of the best of which is that known as the 'Scott Multiple Effect Evaporator.' By means of this apparatus, coupled with a rotary furnace, it is possible to effect recovery of 95 p.c. of the soda, and with a coal consumption equal to 10 cwt. per ton of ash produced.

One form of the evaporating plant is shown in Fig. 6, and may consist of one or more vessels. Each unit consists of an evaporator, the heating surface of which is in the form of tubes of two different diameters so arranged that the liquor which circulates in these tubes does so with considerable velocity, thus exposing a large heating surface. The steam generated in the first effect, working under a pressure of 4-5 lbs., is used to heat the second 'effect' which works under a slight vacuum, and so on for each consecutive unit, with a correspondingly increased vacuum.

The 'black' liquor is pumped up to the first 'effect' and passes through each succeeding 'effect' until it is so concentrated that it will only just flow.

The concentrated liquor is pumped up to a store tank mounted above a roaster, which may be of the flat hearth type or better still, a rotary roaster. The latter is a revolving steel shell provided with steel rails, and supported on steel wheels, some of which act as 'supports' and others as dividers. The inside lining of fire brick is so arranged that a slight slope is given from the feeding end to the discharging end. The concentrated liquor is fed into the roaster at a constant rate, the temperature of the roaster being at white heat. This causes immediate evaporation and firing of the organic matter. The fused sodium carbonate is carried forward to the end of the roaster, and is ultimately discharged as a dark incandescent mass into barrows placed at the end of the furnace. The contents of the barrows are left to burn slowly when the product is almost quite white.

The Varyan evaporator is similar in principle to that already described. An important advantage of these evaporators is the fact that the liquors, excepting while in the incinerating furnace, are not in contact with the products of combustion of the fuel employed. Moreover, the bulk of the water evaporated is recovered in the form of distilled water.

The recovered soda, which, as has been said, is in the form of carbonate, may contain in addition a considerable quantity of potash, derived from the fibrous substances which have been boiled in it; also in the case of straw or esparto, a large proportion, as high as 7 p.c., of silica. It is dissolved in water and causticised by boiling with lime, when almost the whole of the soda it contains is recovered in the form of sodium hydroxide. It should be borne in mind, however, that it is liable to contain various accumulated impurities such as sulphate and chloride, &c., derived from the soda originally employed, and from that which has to be added to make up the loss in evaporation. This loss, together with that due to soda retained in the fibre,

leakage, soda volatilised during calcining, and soda left in the lime mud after causticising, invariably amounts to 5-10 p.c.

It is important that the loss should be made up with as pure a form of alkali as possible.

E. J. B. and W. B.

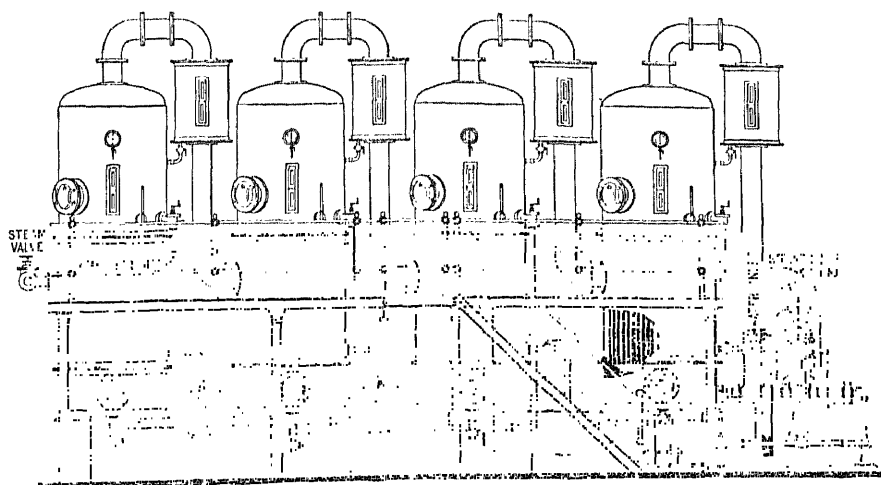
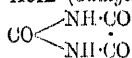


FIG. 6.

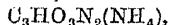
**PAPER-COAL.** A synonym for Dysodile (*q.v.*).

**PARABANIC ACID** (*Oxalylcarbamide*)

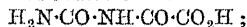


prepared by the oxidation of uric acid with moderately concentrated nitric acid (Liebig and Wöhler, *Annalen*, 1838, 26, 285; Strecker, *Annalen*, 1861, 118, 151; Tollens, *Ber.* 1872, 5, 801), with hydrochloric acid and potassium chlorate, with manganese dioxide and hot dilute sulphuric acid, or with bromine and water; or by oxidising guanine with hydrochloric acid and potassium chlorate (Fink, *Annalen*, 1864, 132, 298); has been synthesised by heating oxamide with phosgene at 170°-180° (*v. Basaroff*, *Ber.* 1872, 5, 477), or by boiling it with phenyl carbonate (Cazeneuve, *Compt. rend.* 1899, 129, 834); by the action of phosphoryl chloride on a mixture of oxalic acid and carbamide, or on oxaluric acid (Grimaux, *ibid.* 1873, 77, 1548); or by distilling the monoxide of nitropyruvil  $\text{C}_2\text{H}_3(\text{NO}_2)\text{N}_2\text{O}$  with bromine and water (Grimaux, *l.c.*; 1874, 79, 1478). Parabanic acid crystallises in flat, monoclinic prisms, soluble in 21.2 parts of water at 8°, and melts and sublimes at 100°. The *hydrate* ( $\text{C}_2\text{H}_2\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$  or  $\text{CO} \begin{cases} \text{NH} \cdot \text{C}(\text{OH})_2 \\ \text{NH} \cdot \text{CO} \end{cases}$ ) is obtained when uric acid is oxidised with nitric acid (sp.gr. 1.3) at 35°-60°, it forms large compact crystals, soluble in 7.4 parts of water at 8°, becomes anhydrous at 150°-160°, and the dried substance recrystallises from water in anhydrous needles (Tollens and Wagner, *Annalen*, 1873, 166, 321; Tollens, *Ber.* 1872, 5, 801; *Annalen*, 1875, 175, 227). Parabanic acid has heat of combustion +212.7 Cal., heat of formation +139.2 Cal., heat of dissolution -5.1 Cal. at 20° (Matignon, *Compt. rend.* 1891, 113, 198); the dissociation constant for N/32 solution is  $0.75 \times 10^{-6}$  (Wood, *Chem. Soc.*

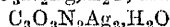
*Trans.* 1900, 1837). Parabanic acid is found in the urine partly unchanged and partly as oxalate (Pohl, *Zeitsch. exper. Pathol. u. Ther.* 1910, 8, 308); it acts on the central nervous system, producing first paralysis, then paralysis and finally death (Lusini, *Corpor* (Lusini, *Chem. Zentr.* 1895, ii, 311, 727, 838). Parabanic acid is a dibasic acid, the *ammonium*



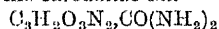
*potassium*  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{K}$  and *sodium*  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{Na}$  salts, prepared by adding alcoholic ammonia or potassium or sodium ethoxide to an alcoholic solution of the acid, are crystalline precipitates converted in aqueous solution into the corresponding salt of *oxaluric acid*



the *mono-*  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{Ag} \cdot \text{H}_2\text{O}$ , and *di-*



*silver salts* exist (Menschutkin, *Annalen*, 1874, 172, 73; Rudinskaja, *J. Russ. Phys. Chem. Soc.* 1885, 278); the *carbamide salt*



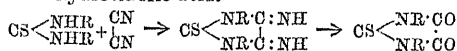
forms flat prisms (Hlasiwetz, *J. pr. Chem.* 1856, [i.] 69, 106).

**Alkyl and aryl substituted parabanic acids** have been prepared by the oxidation of certain purine derivatives, or more generally by the action of alcoholic silver nitrate on the corresponding parabanic acid. These compounds do not yield a precipitate with a cold solution of calcium chloride to which ammonia has been added, but on warming the mixture, calcium oxalate is precipitated (Andreasch, *Ber.* 1881, 14, 1447; 1898, 31, 137). *Methylparabanic acid*  $\text{C}_2\text{H}_4\text{MeO}_3\text{N}_2$ , by oxidising theobromine with chromic acid, or caffeine with bromine, forms transparent prisms, m.p. 149.5°; the *methyl-carbamide salt*  $\text{C}_2\text{H}_4\text{O}_3\text{N}_2 \cdot \text{C}_2\text{H}_5\text{ON}_2$  has m.p. 127°-128° (Maly and Hinteregger, *Ber.* 1881, 14, 723, 893; *Monatsh.* 1882, 3, 85; Fischer and

Frank, Ber. 1897, 30, 2609). *Ethylparabanic acid*  $C_3H_5EtO_3N_2$ , m.p.  $45^\circ$ ; *allylparabanic acid*, m.p.  $140^\circ$ . *Dimethylparabanic acid*, *cholesterophum*  $C_3Me_2O_3N_2$ , obtained by oxidising caffeine with nitric acid (Stenhouse, Annalen, 1843, 45, 371; 46, 229), with chlorine water (Rochleder, *ibid.* 1850, 73, 57), or with bromine water, or by the action of methyl iodide on silver parabamate (Andreasch, Ber. 1898, 31, 138); melts at  $145.5^\circ$  and distills unchanged at  $275^\circ$ – $277^\circ$ , is soluble in 53.4 parts of water at  $20^\circ$  (Maly and Hinteregger, *l.c.*), and its heat of combustion is  $+539.1$  C. Ann. Chim. Phys. [vi.] 28, 70). *acid*  $C_3Et_2O_3N_2$ , m.p.  $46^\circ$ ; *methylethylparabanic acid*  $C_3MeEtO_3N_2$ , by oxidising m.p.  $44^\circ$ ; *methylallylparabanic acid*  $C_3H_7O_3N_2$ , m.p.  $75^\circ$ ; *ethylallylparabanic acid*  $C_3H_{10}O_3N_2$ , m.p.  $66^\circ$ ; *methylphenylparabanic acid*  $C_{10}H_9O_3N_2$ , m.p.  $148^\circ$ ; *ethylphenylparabanic acid*, m.p.  $97^\circ$ .

acid.

**Thioparabanic acids** passing cyanogen gas into an of the thiocarbanide and heating the resulting cyanides with hydrochloric acid.



They are yellow or orange-coloured crystalline and the thioparabanic acids described above have been prepared (Andreasch, Ber. 1881, 14, 1447; 1898, 31, 137).

M. A. W.

#### PARABISMUT *v.* SYNTHETIC DRUGS.

#### PARACONIC ACID *v.* LACTONES.

**PARAFFIN.** *Properties.*—Paraffin is a solid wax-like substance, colourless, tasteless, and odourless, composed of saturated hydrocarbons of the series  $C_nH_{2n+2}$ , with m.p. from  $100^\circ\text{F.}$  ( $38^\circ\text{C.}$ ) to over  $135^\circ\text{F.}$  ( $57^\circ\text{C.}$ ). The higher melting varieties are hard and tough at ordinary temperatures; all are plastic for some interval under their melting-points, and when fused are thin mobile liquids. Paraffin expands considerably in melting. With a wick it is easy to get it to burn with a clear white smokeless flame; but it does not burn readily in the mass. Its flashing-point is over  $350^\circ\text{F.}$  ( $177^\circ\text{C.}$ ).

The sp.gr. varies from 0.790 to 0.940 to melting-point and origin. m.p.  $38^\circ\text{C.}$  had sp.gr. 0.8740; sp.gr. in the melted state, calculated to  $21^\circ\text{C.}$  was 0.795 (Beilby). The sp.heat is 0.694. It is a nonconductor of heat and electricity. It contains carbon about 85 p.c., hydrogen 15 p.c. It is insoluble in water, but soluble in ether, mineral spirit and carbon disulphide. It is characterised by indifference to most reagents, and can resist the action of many of the even when heated.

Paraffin is used in vast quantities for candle-making; the softer quality for miner's lamps, and household-, ship-, and hand-lamps; also for dipping the sticks of matches in place of the sulphur of long ago; and often gets the name of match or miner's

paraffin. The per- of paraffin make it a useful for any purposes, and as day by day it is getting more plentiful and of lower price its applications are extending. It is used for waterproofing cloth, leather, walls, carriages, and wrapping paper; for coating the inside of vessels to prevent the wood giving a taste to the delicate substances in them, such as butter, mineral waters, beer, &c.; for coating metals to prevent rust and decay; for electrical insulation; for splints in surgery, as a medium for salves, for extracting perfume from flowers; for waxing thread, floors, &c., for heating-baths in laboratories, and numerous other purposes.

*Production.*—Paraffin is found native in various forms in the coal and other measures, e.g. as ozokerite (*q.v.*). A hundred years ago and more Uphall Parish and neighbourhood was lighted with ozokerite candles from Binny quarry, and to be used.

into the market as ceresin. Paraffin was first produced in quantity from bituminous shale, and that is still an important source in Scotland, France, and Australia. In Germany it is obtained from the distillation of brown coal. It is now obtained from American, Galician, and other petroleum, but not from that of Baku. In shale oil and petroleum it is associated with liquid and gaseous members of the paraffin and other series of hydrocarbons. Scotch crude oil contains 11 p.c. of solid paraffin, brown coal tar 12 p.c., Galician petroleum 5 or 6 p.c., American 2 or 3 p.c., Upper Burmah and Assam sometimes 12 p.c. or more. For many years Scotland, with a yearly production of 20,000 tons was the principal producer in the world, but now America produces 100,000 tons, and Galicia now puts on the market over 60,000 tons per annum.

Distillation of bituminous shale for liquid products was tried in Scotland by Lord Dundonald as early as 1781, but the world was not ready for it. Previous to  $18^\circ$  had been extracted in the petroleum, wood-tar, and coal-tar, but throughout the world generally it was known only as a chemical curiosity. In France, however, manufacturing it had been attempted on a small scale as early as 1830, and candles proposed and patented in 1845. On the large successful manufacturing scale it was first produced in Scotland from torbanite, and this undertaking at once became well known and influenced the whole world. Later on oil shale was used.

Oil shale is at present worked for oil refining in Scotland, France, and Australia, and shale suitable for the purpose is found in Nova Scotia, New Brunswick, Serbia, Spain, Tasmania, and many other places.

The methods of refining are the same for petroleum, brown coal, and shale oils, viz. fractional distillations alternated with treatments of oil of vitriol and of caustic soda; and the heavy oil when it contains solid paraffin, is cooled and pressed for its separation. A description of the Scotch manufacture is so far typical of all, but shale oil requires much more refining than petroleum. Crude petroleum is obtained directly by boring and pumping, whilst



shale and brown coal have to be mined and retorted to get the crude oil. This extra expense is to some extent compensated for by the production of ammonium sulphate.

There is no hope of the petroleum wells lasting permanently, and the world's stock of it is being rapidly used up. The vast shale fields of the world will before long become of great interest and importance.

#### THE SHALE OIL INDUSTRY.

*Locality.*—At one time there were crude oil works scattered over all the British coal-fields. Now, however, all the oilworks existing in Britain are situated on a belt of the oil shale formation, 6-8 miles wide, stretching from the shores of the Firth of Forth at Aberdeen and Dalmeny 16 miles southward to the east end of the Pentland range of hills at Cobbinshaw. Going due west from Edinburgh for 13 miles lands one in the middle of this tract. Besides this locality there is a regular strike of the shale seams in a narrow strip 10 miles to the east, where the seams lie much closer together. There were workings on it at the village of Pentland. This line is continued to the north side of the Forth and was worked at Burntisland.

The raw material used is a shale, which, while containing not more than 2 p.c. of true bitumen soluble in carbon disulphide, has much organic matter present capable of giving bituminous materials by destructive distillation. It is black or brownish in colour, fine in grain, free from grit, and with brown streak. It is tough, and good samples under the knife curl over in thin shavings, while poorer samples are more friable. Some good foreign shales have not this property of curling in thin shavings. It resists disintegration by weathering. Some shale is 'plain,' having the laminae parallel with the stratification; other shale is 'curly,' side pressure while plastic having crushed it into irregular masses, with irregular surfaces. The amount of shale distilled in Scotland in 1911 was 3,000,000 tons.

*Products.*—The crude oil, in amount about 70 million gallons or 273,500 tons per annum in Scotland, varies in proportion of products according to the nature of the shale and the retorting. The products are:—

1. Shale oil, about 4 p.c. on the crude oil, sp.gr. 0.600-0.750, used as gasoline, motor spirit, solvent for india-rubber, burning in special lamps, &c. Water-white in colour.

2. Burning oil, 20-30 p.c., sp.gr. 0.785-0.830, used for lamps, and for internal combustion engines. Water-white or faint straw tint.

3. Intermediate oil, sp.gr. 0.840-0.865, 10-20 p.c. used for gas-making, gas-enriching, cleaning purposes, oil engine fuel, grease-making, and fuel for the navy.

4. Lubricating oil, sp.gr. 0.865-0.900, about 20 p.c., used for lubricating machinery. Clear yellow colour.

5. Solid paraffin, 10-12 p.c., see above.

6. Still coke, 3 p.c., used as a smokeless fuel for yachts, drawing-rooms, &c., and for electric candles, moulders' blacking, &c. Fixed carbon 95 p.c., ash 0.5 p.c., sulphur 0.4 p.c., volatile hydrocarbons 4 p.c.

7. Ammonium sulphate, about 60,000 tons a year, used as manure, especially for sugar beet growing, and largely exported.

8. The tars, 15 p.c., washed from the chemicals used in refining, are burned as fuel under the stills, sprayed with superheated steam.

9. Permanent gases are produced in the retorting and used as fuel for heating the retorts; and very rich pure gas is got in the refinery in distilling the crude and heavy oils to dryness and is used for illumination, and for fuel purposes under the stills.

The oil products are composed of the paraffin and olefine series of hydrocarbons with a small but definite admixture of naphthenes and benzenes. In the impurities extracted by the chemicals and the distillation are strong bases of the pyridine and quinoline series, phenols, cresols, pyrene, chrysene, and other hydrocarbons more dehydrogenated than the olefines; but the tars have not been thoroughly investigated.

*History.*—At Lyon Playfair's suggestion, James Young started, in 1848, a works in Derbyshire to refine petroleum from a spring found in connection with coal. The supply, some 300 gallons a day, soon threatened to stop, and Young, who supposed that this petroleum had been distilled by a natural process from the coal, set himself to create artificial petroleum by the distillation of coal at low temperatures. He experimented with many varieties, English and Scotch, and found that cannel or gas coals were suitable. He at last discovered the Torbanehill mineral near Bathgate, which proved exactly what was wanted. He took out his patent for low temperature distillation of coal in 1850, and the Bathgate works were in operation before the close of the year. Markets were soon created for lamp oil, which was the principal product, and also for kerosene oil and solid paraffin. Young's lamps, and paraffin oil rapidly became the light of the people all over Britain. He called lamp oil paraffin oil, and paraffin oil, or simply paraffin, is the name yet commonly given in Britain to mineral oil for lighting purposes, whether of shale or petroleum origin. In America and on the Continent the name paraffin oil is applied to the heavy oil which is pressed directly from the solid paraffin. The manufacture proving a great success a good many works were erected throughout Britain during the run of Young's patent, and many were got ready to start on its expiry in 1864, and others were added afterwards. Factories were also started on the Continent, some of them getting the Torbanehill mineral exported to be distilled abroad. Many works were erected in America to work Young's patent and distil the native coals, and adopted his method of refining. Petroleum from oil springs began to be produced in quantity in Pennsylvania in 1859, and these coal refineries were in existence ready for its refining, and helped in the rapid development of the new industry. Coal oil was already well known in America, and lamp oil or kerosene is often yet called kerosene in the States and Canada. In the sixties the exportation of American kerosene to the United Kingdom began and increased

rapidly. The lamp oil fell in price from 2s. 6d. to 1s. 3d. per gallon, and many works had to stop. In 1871 there were 81 works, within two years only 30. The Americans at first exported only burning oil, and the Scotch modified their retorts to produce heavy oil and paraffin, and bought in American residuum to refine it. Soon the Americans took up these branches, and the United Kingdom was supplied with a superabundance of lubricating oil and solid paraffin, and their prices fell also. The ammonium sulphate, a by-product, became the saving of the industry, and the retorts were so modified that its production was doubled or trebled. About 1880 the supply of Peruvian guano, on which farmers had depended for their supply of combined nitrogen, now began to fail, and as a result the price of sulphate rose to £24 a ton, and the number of works was increased. But by 1890 sodium nitrate was imported in such quantities that the price of ammonium sulphate fell to £8 a ton, while burning oil brought only 6d. a gallon; and again there was collapse. The Russian petroleum industry had developed rapidly after 1873, and through time was competing in the English market for lamp and lubricating oils. Later on came competition from Galicia, Roumania, and the East Indies. The Scottish industry has thus had many vicissitudes, times of success with expansion alternating with depression and collapse. When bad times came the weaker concerns ceased to exist, but the stronger ones enlarged their works to cheapen production by the many economies that enlarged output brought. In the sixty years of the industry 120 works have dropped out of existence causing the loss of several millions of capital, yet the yearly production has not declined but rather increased. There are now only seven companies in all, viz. four with refineries, and three which produce only crude oil and ammonium sulphate. In spite of the increased production of combined nitrogen from many new sources such as iron smelting, mondgas, coal coking, and electrical utilisation of atmospheric nitrogen, the demand of farmers all the world over has increased so that the price of ammonium sulphate has remained for a series of years from about £12 to £14 a ton. Shales that not long ago would have been rejected as rubbish are now most valuable on account of the large yield of ammonia, and the exhaustion of the shale supply is indefinitely postponed. Recent enlargement of the Scotch refineries, combined with the usual foreign competition, accentuated by the price war between the two great foreign petroleum corporations, have lowered the price of paraffin products, and the present outlook is discouraging. Further economies are necessary, and the combination of all the companies into one organisation, particularly in the selling department, suggests itself as possible.

The continued existence of this home industry has without doubt kept the light of the people at one-half the price of what it would otherwise have been, and a great deal cheaper than it is at the very gates of many American refineries.

*Materials that have been used.*—Young started the Bathgate works to distil the Torbanehill

mineral (torbanite), called also boghead coal. It yielded 100–130 gallons of crude oil. Volatile matters, 65 p.c., ash 22 p.c. It was a rich shale rather than a coal. The residue left from retorting was not a coke as with coal, but was in thin layers like spent shale, and the crude oil was lighter, viz. sp.gr. 0.9, instead of 1.0 as with coal. It was getting exhausted and too expensive within a dozen years, and shales were used instead, and also some parrot coal. The shales at first tried yielded 45–30 gallons a ton, and those now in use give from 30 to 20 gallons. A 30 gallon shale has about 25 p.c. volatile matter and 75 p.c. fixed, of which 5 p.c. is carbon. The shale or parrot coals from the coal measures produced generally a crude oil having a higher sp.gr., more loss in refining, a thinner lubricating oil, and less solid paraffin than the shales of the shale measures.

**Geology.** The position of the shale measures in Scotland may be seen from the following statement in which the series are arranged in descending order:—

Carboniferous System	Coal measures proper.
	Millstone grit.
	Carboniferous limestone series.
	Calcareous sandstone series,
	in which are the true shale measures.
	Old red sandstone.

The coal measures proper with their many seams of workable coal have seams of shale or bastard cannel coal which were distilled in the early bright days.

Over many ordinary seams of coal there was found a foot or more of suitable material which was kept apart and distilled. It was found, for instance, in connection with the splint and Virtuewell coals, the Musselband ironstone, and Kiltongue coal, in the Coatbridge district. Seams from the true coal measures were worked for oil in Fife, Ayrshire, and Midlothian, as well as throughout the English coal-fields in Yorkshire, Lancashire, Cheshire, and Stafford, and in particular there was for some time a considerable Welsh shale oil manufacture at Leeswood in Flintshire. The position of the Torbanehill mineral itself was near the base of the coal measure not far above the millstone grit.

The carboniferous limestone series with its valuable limestone, coal, and ironstone contains seams of shale and parrot coal that were worked for oil in Lanarkshire and Fife.

But foreign competition and low prices caused complete stoppage many years ago of all oilworks in Britain except those of the true shale measures.

The calciferous sandstone series, in its upper division, sometimes 3000 feet thick, contains all the oil shales worked at the present time. The seams, about twenty in all, vary much in thickness and quality in the different districts and the intervening strata are also variable. The following is a generalised section to show the succession, &c. The gallons are the crude oil, and the lbs. the ammonium sulphate, per ton of shale, as obtained in the modern retorts. The thickness in feet.

Hurlet limestone and coal, a widely known position reckoned the top of the shale measures. Strata, 400 ft. blaes, ironstone ribs, blackband

ironstone, &c. (containing an upper Raeburn Seam at S. Cobbinshaw 100 ft. above the next shale).

*Raeburn shale*, 3-6 ft., 40-55 gals., worked at West Calder and Tarbrax. Strata 190 ft., blaes, ironstone bands, &c.

*Mungle shale*, 2 ft., 35 gals., 30 lbs. Strata 130 ft., blaes, fireclay, ironstone bands, volcanic tuff.

Two feet coal, with a thin shale and ironstone band. Strata Houston marls, 230 ft., thick beds, massive, amorphous, unfossiliferous.

*Addiewell grey shale*, 2 ft., composed largely of entomostraca. Strata 60 ft., blaes, fireclay.

Houston coal, 4-6 ft. Lowest coal that has been worked to any extent in Scotland. Inferior, pyritous, and interbedded with blaes. Strata 150 ft., laminated sandstone, blaes, clayband ironstone.

*Fell's shale*, 3-7 ft. Principal shale of West Calder district, 26-40 gals., 30 lbs. Strata, Broxburn marl, 135-270 ft., limestone immediately under Fell's shale, 3-6 ft., marly clays, cement stone, no sandstone.

*Broxburn grey shale*, 6 ft., 23 gals., 35 lbs. Strata 5 ft.

*Broxburn curly shale*, 5½ ft., 26 gals., 38 lbs. Strata 6 ft.

*Broxburn seam*, 5-6 ft., 30-35 gals., 40 lbs. At Midcalders there are other two seams above these three Broxburn seams, and another 16 ft. below the Broxburn. Strata 400-500 ft. blaes and marl, then the Binny sandstone, then again blaes and marl.

*Dunnet shale*, 4-12 ft., 24-33 gals., 24 lbs. At Oakbank there is a lower dunnet shale. Strata 400-600 ft., sandstone, blaes, lime ribs.

*Barracks shale*. Very variable, sometimes 8 ft., and yielding 22 gals., but generally thinner and poorer.

*Burdie house limestone*. . . . . position. Sometimes 64 ft. 600 ft., blaes and thick sandstones.

*Pumphreston shales*, 5 of them, with about 12 ft. of blaes between each pair, respectively 8, 5, 6, 7, and 4 ft. thick, 16-20 gals., 50-70 lbs.

The lower division of the calciferous sandstone varies from a hundred to several thousand feet in thickness. Sandstones, non-bituminous shales, cement stones, &c., fill up the space until the upper old red sandstone is reached. The Wardie shales (11 gals., 20 lbs.) of this lower division would not pay to work under present circumstances.

The oil shale measures are very much troubled. They are contorted into great waves, sometimes even overlap, and the same seams come to the surface at many places. There are four great faults running E. or N.E. with displacement of 1000-1500 ft., and numerous small faults or branches to the large ones. There are dykes of igneous rock running through the strata; and there are many great sheets of intrusive sill intercalated between the normal strata, sometimes 5 or 6 ft. thick for a long distance, but here and there thickening to a great depth; sometimes keeping the same position for a wide space, then suddenly going higher or lower. The intruded mass has often taken the position of a good shale, utterly

and occasionally retaining some of distillation in calcite-lined cavities in the mass of the sill, as liquid petroleum, solid bitumen, or substance of intermediate consistency like vaseline. Certain sedimentary strata are charged with petroleum and brine. The surface of the country has been partially levelled down in later ages by glacier action, leaving hills with crag and tail where the neck of igneous rock came up.

The calciferous sandstone turns up in a broad band from the east to the west of Scotland, but only in this limited locality of the Lothians has there been the suitable circumstances for the rapid deposit and preservation of the organic material that gives value to the shale. This has been called *sapropel* on the Continent and *kerogen* in this country. It is composed partly of amorphous jelly and partly of microscopic algæ, spores, and other minute forms of life, that seem to have been deposited in a brackish lagoon where there was little circulation and aeration of the water, so that on falling to the bottom they were enclosed in the mud and so preserved from decay. There have been great volcanos in the neighbourhood active during the deposit of this formation which first may have stimulated the minute life by warmth and afterwards by eruption caused their sudden precipitation to the bottom and envelopment in the mud. Dust thrown out by volcanos has formed extensive tuff strata throughout the district. Earthquake or poisonous gases may have caused the sudden death of the fish of the fish beds; and the many thin deposits of chemical limestone may have obtained the heat for the decomposition and precipitation of the bicarbonate from the neighbouring volcanos.

The shales worked in France and Australia belong to the carboniferous . . . . . ferous epoch. Vast deposits . . . . . found in Canada in the upper old red sandstone. The Kimmeridge shale of England belongs to . . . . . Oil shale may be got . . . . . of geological time.

Working is much like coal, pillar and stall, and the pillars removed later. Coal-cutting machines are not used. More is done by blasting in shale mines than with coal, various explosives being used, but mostly gunpowder. Boring for the shots is now done at several places by electrical machinery, a hole being drilled in 5 minutes that takes 45 minutes by hand. M. . . . . pumping water, &c. is now . . . . . electric power, raised by steam. Before sinking a mine or pit in a new neighbourhood it has to be well explored by boring as the seams vary much, and the vagaries of the intrusive sill cannot be foreseen. The workings vary from 0 to 1000 ft. in vertical depth, one pit reaching 1600 ft. A seam is often richer towards the outcrop and poorer as it increases in depth, but not always. There is fan draught as in coal pits. The ventilation has to be good to sweep away the smoke of the shot-firing. Fire damp gives little trouble so that naked lights are in general use.

The manufacture is carried out in two divisions: I. the crude works, . . . . . I. *The crude oil works* . . . . . breaking machines, retorts, condensers, receivers,

scrubbing towers to take ammonia and light naphtha from the permanent gases of the distillation, a tower oil still and ammonia house. The crude works is situated in the middle of the shale field so that much of the shale is tipped into the breaking machine direct from the miners' hutches. It is expensive to convey shale far underground, and so mines or pits are put down all over the field and the shale brought in railway waggons to be emptied by hydraulic machinery into the breaking machine. If shale lies 5 miles or more from the refinery a crude works is put up there and the crude oil sent to the refinery by rail in tank waggons.

The breaking machines consist of two strong-toothed cylinders between which the shale is broken into pieces about 4-6 in. square. One machine with cylinders 3 ft. diameter and 4½ ft. long puts through over 500 tons in a day of 8 hours. The cylinders are of cast iron 3½ in. thick with malleable steel teeth 2½ in. diameter and projecting 4½ in. outside the cylinder. The teeth of the one cylinder fall between the teeth of the other, and the clearance is self-adjusting 0-1 in.

**Retorting.**—The broken shale falls into hutches on rails holding about 18 cwt., to be taken by endless rope up an incline to the top of the benches and emptied directly into the retort hoppers. The retort hoppers are often so large that filled by day there is sufficient supply for all night. After distillation and passing down through the retort the spent shale falls into a hopper below, which is emptied at intervals, by day and night into iron hutches to be conveyed by endless rope or chain to the top of the spent shale bing.

Retorts are arranged in two rows in benches of 44-66 retorts. The distillation is upwards, and along the top of the retorts on each side

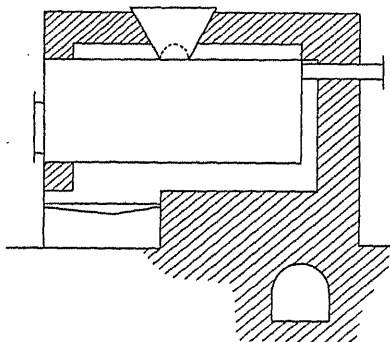


Fig. 1.

there is fixed the main to carry off the products of distillation. The exit from retort to main is 7 in. diameter and the main itself 30 in.

The first retort used by J. Young in 1850 was an imitation of the horizontal iron gas-retort of the time, but worked at as low a temperature as possible. Young soon adopted a vertical retort, but other works continued to use the horizontal type with improved arrangements until 1880 (Fig. 1).

The old vertical retort (Fig. 2), a cylinder about 1½ ft. in diameter and 10 ft. long, had a

bell-hopper above for charging, and a water-lute below through which the spent shale was raked. It was charged at intervals of an hour, and a corresponding quantity of spent shale was withdrawn half an hour after the charging. Vertical retorts, improved in form and setting, oval in section, and lengthened to 15 ft., were

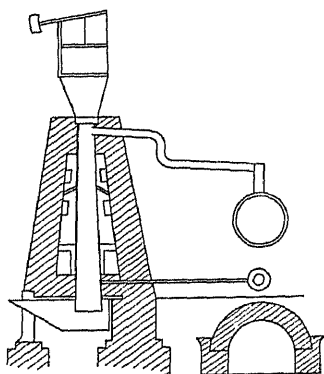


Fig. 2.

in use in some works until after 1880. About 1860 steam had been introduced into the bottom of the retort. It moderated and transfused the heat, and swept the oil vapours rapidly out of the hot region, and the crude oil was improved in quantity and quality. These retorts were fired by coal, and the coal furnace heated three retorts on each side of it. They were often overheated, spoiling the oil and destroying the retort. Young recommended 600°-700°F., but old vertical retorts sometimes reached 1200°-1500°F. as measured by Siemens water pyrometer. The result was thus dependent on the care of the men.

Many forms of retorts were patented. W. Young in 1867 tried a retort with gas-jacket around the metal retort. It was not a success, but it proved that a great improvement in the quality of the crude oil could be effected by gentle heating. The spent shale of the early retorts contained about 12 p.c. carbon, and a large proportion of the nitrogen. W. Young in 1872 attempted to utilise the spent shale for fuel with a gas lute between the products of combustion of the spent shale and the products of distillation. It required too much care in its management. N. M. Henderson in 1873 patented an arrangement by which the spent shale was dropped into a furnace below and served as fuel for the next charge (Fig. 3). This was an intermittent process, and held 18 cwt. shale, and

every 16 hours. Four retorts were in an oven over one furnace and one was dropped every 4 hours. The fuel bill was greatly reduced, and the power to overheat was taken from the men and a greatly improved crude oil was the result. This retort was widely adopted for some time. The distillation was downwards.

The modern type of retort was the invention of George Beilby and William Young, experimenting at first independently and afterwards in partnership. The Young and Beilby retort, 1881, Fig. 4, was a continuous working one,



gas, ammonia water, and spent shale. The great hills of spent shale are a conspicuous feature in the shale districts. The spent shale of the retorts previous to Henderson's 1873 patent contained 10-12 p.c. carbon and a large proportion of the sulphur. It gave trouble in the great heaps or bings by igniting spontaneously and burning quietly, giving off volumes of fumes containing  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . The well-exhausted spent shale of the present day is free from that nuisance. The original shale contains  $1\frac{1}{2}$  p.c. sulphur.

The crude oil of the old vertical retorts was dark and tarry, sp.gr. 0.880-0.895. Henderson's 1873 retort produced a crude oil, sp.gr. 0.865-0.870, which yielded  $2\frac{1}{2}$  p.c. more total products, all of improved quality, and contained  $2\frac{1}{2}$  p.c. more solid paraffin. The Young and Beilby

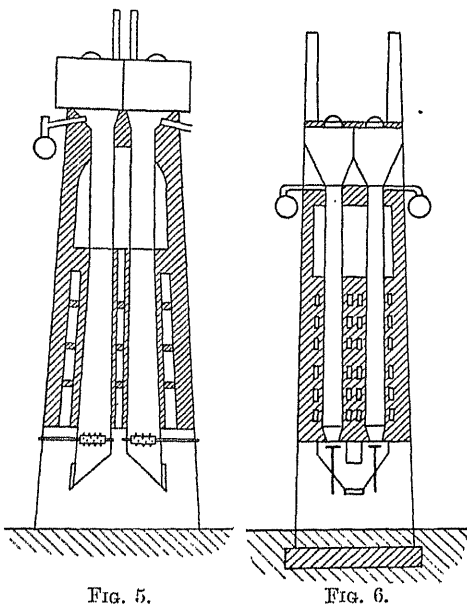


FIG. 5.

FIG. 6.

retort gave a slightly increased quantity of crude oil and of solid paraffin. The Bryson retorts are worked at a high temperature to produce a crude oil of 0.880 sp.gr. rich in paraffin but somewhat difficult to refine. The present Henderson retorts are worked at a mild temperature to give a crude oil of sp.gr. 0.868 and of good quality.

**Retort condensers.**—The vapours are led first through a tubular tower in the pipes of which the water for the steam boilers is heated; then through condensers. Many forms have been tried, but the universal arrangement now is great benches of 4-in. pipes, cooled by the atmosphere, and sometimes having a little water sprinkled over them. The pipes, 27 or 36 ft. high, are arranged vertically and fixed below in two rows into chests, two dozen pipes for the descending gases and the same number for the ascending, with arched connections at the top. There is about 100 lineal feet of this piping, or 100 cub. ft. of surface, for each ton of shale put through per day per retort. The water and oil condense separate from each other at

once in a box called a separator and are run into their several receiving tanks. The gases pass from the condensers through scrubbing towers; one or two in series of water towers to catch the ammonia, and one or two of oil towers (oil sp.gr. 0.850) to catch the last of the condensable spirit. The gas is then caught by a fan which sucks the gases through the towers and condensers and pushes it forward to the retort flues where it is burned. The fan causes a suction equal to 6 in. of water, and this vacuum passes back to the retort, being equal to  $\frac{1}{2}$ -2 in. water at the retort exit. After burning in the flues of the retorts the products of combustion are passed off into the atmosphere by little chimneys at the top of the retorts, or are gathered into a common flue and taken to a tall chimney stalk. J. J. Coleman had a method of extracting gasolene from the permanent gases by cold and pressure. It was expensive, and has not been used for many years. The filling for the scrubbing towers now used is very various.

**The ammonia water distillation** is carried out in column-stills (Fig. 7), generally of circular section, and filled with a dozen or more trays. The feed water, after being heated in an exchanger by the spent ammonia water, travels down the column from tray to tray, while steam introduced at the bottom bubbles through each tray and liberates the free ammonia. Milk of lime is pumped into one of the trays near the bottom to release the fixed ammonia. The ammonia gases are led from the top of the still down to a 'cracker box' or saturator containing dilute sulphuric acid, and into which oil of vitriol is thin stream, and the ammonia perforated lead pipes laid near the bottom. The bottom is sloped and the solid ammonium sulphate formed is swept into a well from which it is lifted by a steam injector and thrown into a conveying tub above, and the liquor lifted drains back into the cracker box,

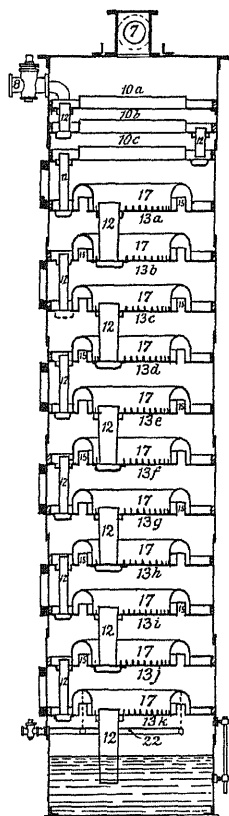


FIG. 7.

while the salt, after draining, is emptied into a bin. Here it drains or dries for a week before being ready for bagging for the market. The salt is now often obtained from the saturator when it is emptied once.

Acid water recovered from the acid tar of the oil refinery is saturated with ammonia in a somewhat similar manner. The saturation has to be complete, so as to separate the impurities. The excess of ammonia which escapes is caught in a vessel at a higher level containing the next charge of acid. The basic tar rises to the surface carrying with it the arsenic and the iron oxide, and is used as fuel. The solution of ammonium sulphate requires to be evaporated down. The oil of vitriol in the cracker box, previously described, requires diluting, and this solution is used. Any solution left is evaporated down in a vacuum pan something like those used for sugar, and the salt is sent into a centrifugal machine to dry it.

The steam from the cracker boxes containing  $\text{CO}_2$  and some  $\text{H}_2\text{S}$  is passed into the shale retorts along with steam from the steam boilers.

The spent water has a strong smell and dark colour. It is pumped up and distributed over the hot spent shale on the bing where some is evaporated and the rest is filtered and passes off at the bottom of the heap, clear, colourless, and almost free from smell. Other dirty water is clarified in the same way.

In Germany there are a dozen brown coal distillation works, all in the Halle region. Over a million tons are distilled annually from 1300 retorts, each 60 feet long, of crude oil, sp. gr. 0.825–0.830, and paraffin wax. The burning oil, sp. gr. 0.825–0.830, requires special burners, and much is now used for internal combustion engines. The heavier oils, called yellow oil, red oil, and paraffin oil are used for internal combustion in Diesel engines, and for gas making, gas enriching, and liquid fuel, and not much for lubricating. The retorts (Fig. 8) are vertical and of circular section. The outer wall is of firebrick surrounded by heating flues. The inner wall is formed of iron rings with openings between them, and with openings down continuously in the space between the iron rings and the brick wall, and the central tube formed by the flues receives and carries off towards the condenser the product of distillation. The retorts vary in size. A cylinder 16½ ft. high and 6½ ft. wide puts through 20 tons of brown coal in 24 hours. The heating is done by coal, by gas, or by a mixture of both.

In France shale is distilled in three oilworks, one at Autun (Saône-et-Loire) and two at Bruyère-les-Mines (Allier). 160 retorts are in operation, distilling 150,000 tons yearly, and producing 2,440,000 gallons crude oil. The newer retorts are of the Young and Beilby type. The yield of crude oil is about 17 gallons to the ton, sp. gr. 0.912, and contains less than 3 p.c. paraffin. The crude oil is difficult to refine, and the burning oil is rather poor in quality. The gas oil is in large proportion. The lubricating oil, however, is of very good quality. The ammonium sulphate varies from 13 to 22 lbs. per ton. Two companies turn out coal from the shale mines and the other one works torbanite to sell to the gasworks; none work shale alone.

In Australia little shale is being distilled at the present time; but two large companies are erecting retorts and refineries in New South Wales, about 130 miles from Sydney. From the mines are to be got shale, torbanite, and common coal. The mining is mostly done on the long-wall system, and no explosives used. The shale expands whenever the pressure is removed from it, and when undermined by the pick it soon falls down in pieces.

11. *The refinery* . . . . . distillations with fractionation . . . . . products; treatments with oil of vitriol and caustic

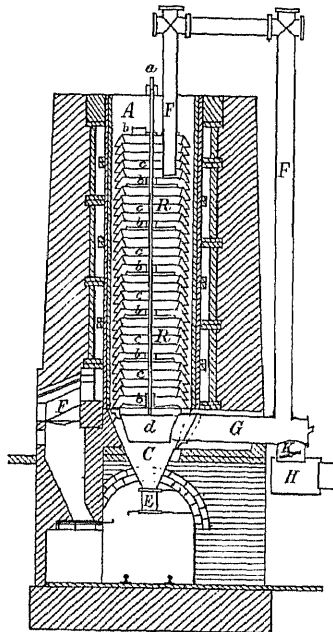


FIG. 8.

soda; the recovery of the chemicals and the preparation of the tars for liquid fuel; cooling and refrigeration of the heavy oil, and filter-pressing to separate the liquid from the solid; and the sweating of the paraffin for its refining. Associated with the refinery is the despatch department with the oil-filling into barrels and railway tanks.

The stills are built in great benches with rows of high tanks built on roundels of circular brickwork, from which the oil flows by gravitation into the stills, and rows of tanks at a low level to receive the distillates. The system used by all the works is Henderson's continuous process (see Fig. 9) or a modification of it. There are cylindrical boiler-benches, each other, or sometimes . . . . . for the crude oil, connected together into a series through which the oil flows continuously, distilling off a fraction from each still, and venting finally into one of a group of residue stills. By means of a pipe within a pipe the oil flowing from the charging tank is heated by the vapours distilling from the second boiler of the series, and is landed hot inside the front of the first still. It travels from front to back,

distilling off the lightest oil, which is condensed in a worm tank condenser. The oil not distilled is taken by a pipe and landed inside the front of the second still of the series, and it travels from front to back distilling off a second and heavier fraction; and on it goes through other boiler stills it may be, until at last the residue oil is passed into a still with pot-shaped cast-iron bottom. These stills are connected and has a fire applied and steam passed through the still until all the air is blown out, so as to prevent explosion. Then the oil from the last boiler still is run in for some hours until the residue still is sufficiently loaded when the oil is shut off from this still and turned into another one. The disconnected still is then distilled to dryness and coked. There are safety valves on the residue stills in case the condenser should choke up with solid paraffin. At first the residue stills were suspended near the bottom of the boiler stills to catch any coke or dirt in circulation; but these have been long disused. In all the distillations steam more or less superheated is passed into the distilling oil as it lowers the boiling-point and helps to carry the vapours over into the condensers. The first or crude oil distillation is meant to be to some extent a destructive one. If the chemical treatments with acid and soda were given direct to the crude oil the loss would be great; or if too much steam is used the oil distils over unchanged with the same result. So the steam is limited for the first distillation and also near the end of the second; but for the third distillation of the heavy or lubricating oil excess of steam is used: it helps to keep the viscosity of the oil high. In the lubricating oil distillation also dry caustic soda is put into the still, 2-5 lbs. per 100 gallons of oil. The condensers are coils of pipes laid in square iron tanks, carrying the vapours downwards, and cold water is passed into the bottom of the tank outside the pipes and overflows hot at the top, and the flow of water is regulated to suit the volatility and quantity of the distillate. The condensed oil from the bottom of the condenser is drawn off by a bend of 8 in. depth on its way to the receiver, but before the bend a pipe rises vertically to take away the gases to prevent them being disagreeable or dangerous at the worm end. The gases used to pass into the atmosphere some yards up, now they are all caught and used for fuel or illumination. They are very rich and, from the second distillation especially, very pure. At coking of the residue stills and approaching the coking, torrents of permanent gas containing some light spirit are given off. Each works had its own method of catching the gases. In Henderson's system the gases are caught by a suction pump through a lute in a main common to a whole bench, the suction being regulated so as not to suck air from the bend of the oil exit.

In the first distillation many residue stills are required, in the later ones the distillation is mostly done in the boiler stills.

**First distillation.**—The crude oil is sometimes distilled from a series of boiler stills of this section (Fig. 9). The stills are horizontal cylinders 7 ft. diameter by 19 ft. to 9 ft. by 30 ft. are used, the charge being 200-4000 gallons.

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The boiler stills are connected sometimes two in a series, sometimes three; or occasionally a central charging still supplies a boiler still, or even two, at each side. In all cases the tails run to residue stills. When two boilers are in a series, the distillate of the first is 0-760-0-770, of the second is 0-820-0-850,

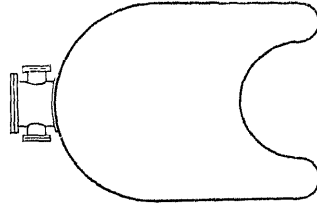


Fig. 9a.

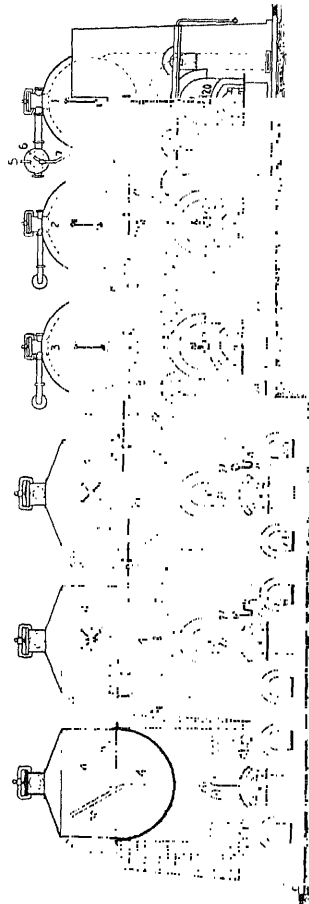


Fig. 9.

while the third in the series, the residue still runs from 0-850 or so when first connected to 0-930 or higher at the end of the distillation. At the end of the residue still distillation there comes over a yellow viscous product called still grease or chrysene which is used for grease making, or for liquid fuel.

For an output of 50,000 gallons a day 4 or 5 boiler stills are required for the crude oil



distillation with about 22 residue stills of 2000 " " " " each. The residue stills are connected to distil to dryness. The still coke is copious and valuable.

The distillate of the first boiler still is kept apart as *green naphtha*, the distillates of the others, boiler stills and residue stills, are generally run together as *green oil*.

*Treatments.*—The green naphtha gets 2 p.c. oil of vitriol and is stirred mechanically, the black tar settled and run off, and the oil is run off into another vessel where it gets stirred with about 1 p.c. of caustic soda solution of 1.3 sp.gr. The naphtha is then ready for another distillation with steam alone, and after that it is colourless, but generally gets another treatment with acid,  $\frac{1}{2}$  p.c., and caustic soda and a finishing distillation, to improve the smell. Distillates are sometimes separated as light as 0.660, but the usual gravities are between 0.700 and 0.750, 0.700-0.720 being sold as motor spirit, and the higher gravities for solvents, &c.

The green oil, sp.gr. 0.855, gets a 2 p.c. treatment with oil of vitriol, the black tar settled and separated and the oil run into another vessel, where it gets 1 p.c. of caustic soda solution, and after settling and running off the tar, it is ready for another distillation. All the stirrings, except for the naphthas, are done by compressed air. The green oil is stirred with the chemicals in large vessels, 30,000-40,000 gallons capacity, cylinders on end with cupped bottom into the centre of which the air is pressed. In the later stirrings the vessels are sometimes horizontal cylinders with the air distributed along the whole length of the bottom. After the stirrings the vessels are closed tight and the air pressure put on the surface to send the oil up into the charging tanks for next distillation. Sometimes the oil is pumped up.

*The second or green oil distillation.*—For a 50,000 gallons a day of crude oil, five boiler stills are required, two receiving the charge and the other three in series, and the tail to residue stills of which there may be ten or more.

1. The distillate of the two charging stills is about 0.800 sp.gr. It requires  $\frac{1}{2}$  p.c. oil of vitriol and caustic soda, and a final distillation before the finishing treatment.

2. The second boiler in the series has sp.gr. about 0.815. It sometimes gets two treatments of  $\frac{1}{2}$  p.c. oil of vitriol and caustic soda and two distillations before it is ready for the market, sometimes only one treatment and distillation.

3. The third boiler distillate is about 0.840, and after the paraffin is extracted is ready for market as gas oil or fuel oil of 0.850 sp.gr. Sometimes it is treated and distilled with finishing treatment for intermediate products.

4. The fourth boiler distillate and the distillate of the residue stills run together, give heavy oil containing paraffin, which, after separation of the solid paraffin as afterwards described, is *blue oil*. This gets 1 p.c. oil of vitriol and caustic soda, and is distilled again and fractionated into the *lubricating oil*, sp.grs. 0.865, and the *motor oil*, sp.gr. 0.895 when the paraffin is again extracted after chilling to a very low temperature. The blue oil distillation is sometimes carried out at once in 5000 gallon pot-stills (see Fig. 10) with dry caustic soda and

excess of steam, sometimes it gets a concentration by passing through two boiler stills and the residue distilled in the pot stills with caustic soda.

The crude oil and green oil residue stills and often the lubricating oil stills are as shown in Fig. 11. Different works have somewhat different distilling arrangements and treatments, and even the same works is always changing somewhat to suit circumstances.

*Finishing treatments.*—Burning oil is treated with 1 p.c. oil of vitriol and weak caustic soda solution of about 1.04 sp.gr., and after settling with a little caustic soda solution of 1.33 sp.gr. is filtered through a filter press with paper instead of cloth. It is nearly water-white.

The heavy oils are treated with 2-4 p.c. oil of vitriol according to gravity, are settled all night, then finished with solution of sodium carbonate, as weak caustic darkens heavy oil, and after settling bright pumped to the filling tanks. It sometimes requires two or more days to settle the heaviest lubricating oils to brightness, and the *settling method* has been tried for rapid settling, the sodium carbonate tar is run off, open steam is blown in until boiling freely through the oil, then settled—and it settles rapidly at the high temperature—and the soda water is run off. Finally, air is blown through the oil, and it is bright. The soda tar of the finishing treatments is white.

The vitriol tar is washed with hot water, stirring the mixture with air and settling. This is done twice. The water seizes the sulphuric

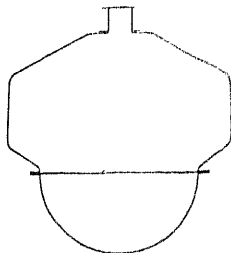


FIG. 10.



FIG. 11.

acid, and sets free the tarry bases. These are settled free from water, and burned under the boiler stills, &c., sprayed with superheated steam. The recovered acid is sent to the sulphate house to get saturated with ammonia as already described.

*Separation of the solid paraffin.*—One method is: The heavy oil containing solid paraffin is air-cooled in shallow tanks in covered sheds open to the wind, and in long cylinders with an inside stirring paddle. After this it is transferred to a cooler which is a tank divided into 6-in. wide spaces for the paraffin mass by 1-in. partitions containing circulating brine of calcium chloride from an ammonia freezing machine. The chilled mass is then separated from the partition by a screw conveyor. The mass lies in the cooler, for 12-20 hours, according

to sp.gr. After being broken up by a mechanical stirrer the mass is passed with considerable pressure through filter presses. The cakes of paraffin scale dropped from the filter-presses sometimes after melting up and recrystallising are sent direct to the sweating stoves without pressing in hydraulic plate presses. In other cases it is plate-pressed to separate the last of the oil.

Another method is: The mixture of heavy oil and paraffin is cooled in a tower by air current, then passed into a long vessel containing a stirrer where it is cooled by a cold-water jacket, afterwards passed into a cooler with stirrer where it is chilled by a jacket of the cold oil from the filter presses, then at last into a tube which may be vertical or horizontal, 17 in. diameter, with a scraper inside surrounded by a wider tube containing ammonia gas which is connected to the vacuum of a suction pump. The paraffin mass thus gets the final refrigeration and passes under high pressure from a pump direct to the filter-presses. The separated oil on its way out chills the oil coming in as stated and passes to a tank to be worked up for lubricating oil. The solid paraffin falling from the filter presses is broken up and conveyed by archimedian screw into the plate-press house, where it is pressed in cloths in hydraulic presses, and the last of the oil expelled. After this the paraffin is ready for sweating.

This direct method of cooling is more economical of power, and although gradual as much as possible, yet the sudden chill at the end causes some paraffin to separate in the amorphous state, and more filter presses are required than with the more gradual cooling with the brine. The brine-cooled paraffin is more crystalline, and therefore the liquid separates from the solid much more readily in the filter presses.

Paraffin is refined by a sweating process. Cakes of paraffin made by cooling and crystallising the melted solid are heated up gradually, when the oil and soft paraffin sweat out carrying

The trays are first filled with water up to the level of the wire-gauze shelf from a pipe at the end, which has a cock to each tray; then 2 or 3 in. of liquid paraffin are run on the top of the water. The great end doors of the chamber are open, and large apertures in the roof so that cooling takes place by natural draught. Sometimes artificial wind from a fan such as is used for mines is applied. When the paraffin is cooled and solidified, the water is run off from below, leaving the great cakes lying on the gauze shelf. By turning a large screw the trays are slightly tilted to help the draining. The doors are shut, and spent steam from pumps and engines is turned into heating pipes ranged up the sides of the apartment, and the temperature gradually rises. The oil and softest paraffin gradually drain out from the hard crystals, and the sweatings are fractionated into receivers according to setting or solidifying point and colour. When sufficiently sweated, live steam is turned on to pipes which support and separate the trays, and the refined wax is melted and run out into its own tank. Semi-refined wax is got by one sweating, and a repetition of the sweating produces refined wax; sweating in itself being sufficient. But sometimes the refining is finished by melting the semi-refined wax, mixing 33 p.c. of spirit of sp. gr. 0.735, cooling into cakes and pressing them, folded in cloth, in hydraulic plate presses. The extracted wax is of a pale yellow colour.

The refined wax is then moved by steaming. Sweatings are themselves sweated at a lower temperature to get low melting-point waxes.

N. M. Henderson has adopted another method of sweating (see Fig. 13). The plant is cheaper, easier to erect, and more economical of space, and it gives a more thorough separation of oil from paraffin and a larger yield of finished wax. A cylinder 7 in. diameter is fixed concentrically within another of 17 in. diameter.

Both are of thin iron, 9 ft. long, and fixed vertically. The centre one is open to the air, both at top and bottom. The outer one has a bottom with outlet pipe and cock, and also a false bottom a few inches up. Around the inner cylinder there are three plies of wire gauze. Water is run into the cell up to the false bottom, and the cell then filled with melted paraffin. After cooling in the same manner as the tray stoves, the water below is run off, and suction is applied to the bottom of the cells by a steam injector on the exit pipe common to a row of cells. The doors are shut and steam put on pipes laid below, and the sweatings find their way through passages formed at once by the heat among the layers of gauze. It has been proposed to expedite the operations by taking the chilled cakes falling from the filter presses, breaking them up and transferring at once to the cells, where the oil is sucked away before the cold paraffin reaches the atmospheric temperatures. The oil is free from dissolved

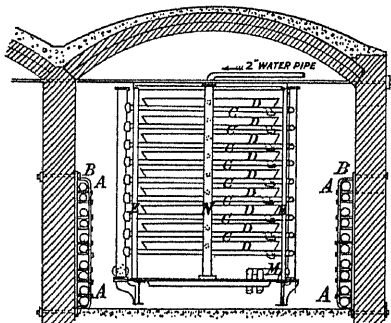


FIG. 12.

the colouring matters along with them. N. M. Henderson's method is the only one used in Scotland, and it is in general use over all the world (see Fig. 12). In a great oblong chamber are built nine tiers of iron trays, in two stacks, making 18 trays in all. They are 6 in. deep, with a wire gauze shelf fixed 2 in. above the bottom.



FIG. 13.

paraffin. This saves the time and expense of melting up and recrystallising.

A double stove of 18 trays takes a charge of about 16 tons. Into the same space 144 cells are placed to hold more than twice the amount of paraffin.

In every case the final process is stirring the melted paraffin with 1 or 2 p.c. char (got from the old method of cyanide making) for 15 minutes, then at once, without settling, pumping the mixture first through a cloth filter-press, and then through one mounted with filter paper. These catch the char, and the wax is ready to run into cakes for the market, or direct into the candle-house tub. Long contact between char and wax is to be avoided for soon the melted wax begins to take up the colour again. The char retains a proportion of wax. This is recovered by a still like a Soxhlet apparatus on a large scale. If the paraffin is thoroughly washed out, the char, when retorted, is as good as at first; but  $\frac{1}{2}$  p.c. of paraffin left in spoils it.

Two of the refineries have candleworks. They supply some wax to other candlemakers, but they also buy much foreign wax to convert into candles besides the bulk of their own production.

Two of the refineries make oil of vitriol for their own use. All recover sulphuric acid from the vitriol tar and use it for making ammonium sulphate. They also recover a proportion of the soda they use.

There are rows of tanks to stock all grades of oil, especially vast tanks to store burning oil for winter use, and Admiralty fuel oil, and they are connected by pipes with taps in the filling houses to run the oils into barrels or railway tanks, or into drums, or tins for cases.

There are tradesmen's shops, wherever needed for mines or works, for smiths, fitters, joiners, plumbers, &c., and also saw-mills, steam-hammers, box-making machinery, and other necessities and conveniences. About 10,000 men in all are employed.

The history of retorting, with many figures, is given by Beilby (J. Soc. Chem. Ind. 1897, 876); and in the same journal, 1897, are described the more modern retorts (Henderson, 981; Crichton, 988; and Bryson, 990). Refining is described (J. Soc. Chem. Ind. 1889, 100) with continuous distillation, &c.

**PARAFFINIC ACID**  $C_{23}H_{47}COOH$ , was obtained by Pouchet (Bull. Soc. chim. [ii.] 23, 111) by oxidising solid paraffin with nitric acid; m.p.  $45^{\circ}$ – $47^{\circ}$ .

**PARAGUAY TEA or YERBA DE MATÉ**, commonly known as *Maté*, or *Jesuits'* or *St. Bartholomew's tea*, consists of the dried leaves and shoots of *Ilex paraguayensis* (A. St. Hil.) (an evergreen related to the holly) and other small trees of the same genus, growing in the mountain woods (known as Yerboles) of Southern Brazil, Argentina, and Paraguay. It is also grown in plantations and is now used as a common beverage by over 50 million of the inhabitants of the South American republics, but has not yet gained favour in Europe, although its use is increasing, especially in France.

The trees are usually about 15 feet high, but occasionally attain a height of over 30 feet. The leaves are from 4 to 6 inches long, lanceolate, with finely serrated margins, and slightly

obtuse apex. The midrib and its branches (the so-called 'veins' or 'nerves') are very prominent on the under side of the leaf. As in ordinary tea, the 'veins' meet before reaching the margin, and the stomata, which are nearly circular, are very numerous.

In the preparation of *maté*, whole branches, together with the twigs and leaves, are cut down, dried and roasted on iron gratings over a wood fire until the proper flavour is developed, then beaten with sticks and the fragments of leaves and twigs roughly ground to a very coarse powder to form the *Yerba de Pulos* of the Spaniards or *Caa-Guaza*. Other and superior grades known on the South American markets are *Caa-Cuyas*, derived from the young leaf-buds, and *Caa-Miri*, which consists of the unroasted leaves freed from their tough fibrous veins and midribs.

The infusion is made by pouring boiling water directly into the cup containing a quantity of *maté* with a little sugar and sometimes lemon-juice, and is imbibed while very hot through a *bombilla* or tube perforated at the bottom or provided with wire gauze to prevent the passage of solid particles of the tea.

It is said to have valuable restorative qualities after violent or prolonged physical exercise, due no doubt in part to the presence of caffeine or theine which, however, is present in smaller proportion than in ordinary tea (*g.v.*), but its effect is narcotic rather than stimulative. It also possesses mildly aperient and diuretic properties.

The amount of caffeine found in *maté* by different observers varies greatly, but trustworthy analyses do not show much more than 1 p.c. The proportion of tannin is also small, being about 1.5 p.c. on an average, and in this respect *maté* is claimed to have an advantage over ordinary tea, as well as from the fact that it is less affected by variations in climatic conditions. The tannin is peculiar in character, as it does not precipitate potassium-tartrate of antimony nor tan leather.

J. C.

**PARALACTIC ACID** *v.* LACTIC ACID.

**PARALDEHYDE** *v.* ALDEHYDE.

**PARAMOL** (*o*-amino-*m*-hydroxylbenzyl alcohol),  $C_6H_4(OH)(CH_2OH)NH_2$ , is a photographic developer, the action of which is intermediate between the developers of the phenol class and the amidophenol class (Eichengrün, Zeitsch. angew. Chem. 1901, 14, 1070). It is soluble in 12 times its weight of water, gives a bluish negative, and can be used for negatives, positives, and papers (Jahr, Brit. J. Photogr. 1902, 49, 32).

**PARANEPHRIN** *v.* SYNTHETIC DRUGS.

**PARAPHENYLENE BLUE**. This dye comes into commerce in three shades, which are designated respectively G, R, and B. They belong to a class of dyes obtained (according to Eng. Pat. 10134, of 1886) by heating paraphenylenediamine (or its homologues) with certain amino-azo-compounds—*e.g.* aminoazobenzene.

Paraphenylene blue R dissolves easily in water with a reddish-blue colour. Hydrochloric acid produces no change in the aqueous solution; but sodium hypochlorite, freshly precipitates the dye in the form of a dark-blue precipitate. Tannic acid, in presence of sodium acetate, yields a blue precipitate, and the liquid is rendered colourless.

The boiling aqueous solution yields a black precipitate with potassium dichromate. The reactions shown by the other shades are similar. On wool, paraphenylen blue dyes direct in presence of a small quantity of acid. On cotton it is fixed by means of tannin and tartar emetic. The shades obtained resemble those produced by methylene blue. When chromed after dyeing the shades become considerably darker (J. Soc. Chem. Ind. 7, 561).

#### PARAROSOLIC ACID *v.* AURIN.

**PARAXANTHINE**, 1:7-dimethyl-2:6-dioxypurine  $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \text{CO} \cdot \text{NH} \cdot \text{C} \cdot \text{N} \end{array} \text{CH}$ , was discovered by Thudichum (Ann. Chem. Med. 1879, 1, 163; Compt. rend. 1888, 106, 1807; by Salomon (Ber. 1883, 16, of which it is a normal constituent, and occurs to the extent of 1.3 grm. per 10,000 litres (Salomon, Virchow's Annalen, 1891, 125, 554; Salomon and Krüger, Zeitsch. physiol. Chem. 1898, 24, 364); and it is found together with other methylxanthines in the urine of dogs and rabbits that have been fed with caffeine (Krüger, Ber. 1899, 32, 2818, 3336).

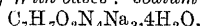
Paraxanthine can be prepared synthetically from theobromine (3:7-dimethylxanthine) by the following series of reactions: theobromine is converted by the action of phosphoryl chloride into ; this on treatment and subsequent methylation yields 2-chloro-6-oxy-1:7-dimethylpurine, which is converted into paraxanthine by heating with hydrochloric acid (sp. gr. 1.19) at 125°–130° (Fischer, Ber. 1897, 30, 2400). Paraxanthine can also be prepared by reducing with hydrogen iodide and phosphonium iodide 8-chloroparaxanthine obtained from 1:7-dimethyluric acid by the action of phosphoryl chloride at 135°–140° (Fischer and Clemm, Ber. 1898, 31, 2622); or by the action of boiling water on 8-chloro-3-chloromethylparaxanthine obtained by heating caffeine with phosphorus chloride and phosphorus 162° (Fischer and Ach, *ibid.* 1906, 39, 423).

Paraxanthine crystallises in six-sided monoclinic plates, m.p. 298°–299° (corr.); in some preparations the crystals become cloudy or whitish at 110°, owing to loss of water of crystallisation, whilst others, isomorphous with them, remain bright (Salomon, *ibid.* 1883, 16, 195; Chem. Zentr. 1884, 490; Zeitsch. physiol. Chem. 1890, 15, 319). Paraxanthine is insoluble in alcohol or ether, dissolves in hydrochloric or nitric acid, or in ammonia; it is sparingly soluble in cold, more readily so in hot, water; at 40.1° 1000 c.c. of water or 1000 c.c. N/10 hydrochloric acid dissolves 1.06 and 1.17 grm. of paraxanthine respectively; the aqueous solution is neutral, and the basis dissociation constant is  $3.29 \times 10^{-14}$  (Wood, Chem. Soc. Trans. 1906, 89, 1842).

The action on frogs paraxanthine, theobromine, or caffeine, affecting the central nervous system and the muscles, and producing creeping movements, then the disappearance of all spontaneous activity and complete abolition of reflexes; the lethal dose is 0.15–0.2 per 1000 of the body weight. On mice the drug produces paresis of the hinder extremities, increase of reflex activity producing tetanus, the lethal dose is

2–4 times as large as for frogs (Salomon, Zeitsch. physiol. Chem. 1889, 13, 187). Paraxanthine acts as a diuretic when administered to rabbits (Ach, Chem. Zentr. 1900, ii, 688), and is excreted partly unchanged and partly as 1-methylxanthine (Krüger and Schmidt, Ber. 1899, 32, 2677).

#### Salts. (1) With bases: sodium salt



sparingly soluble crystalline compound, melts above 300°; the corresponding potassium salt has a higher melting-point (Salomon, *ibid.* 1883, 16, 195). (2) With acids: the hydrochloride  $\text{C}_7\text{H}_7\text{O}_2\text{N}_4 \cdot \text{HCl} \cdot \text{H}_2\text{O}$  forms rhombic plates, dissociates in aqueous solution and loses HCl and  $\text{H}_2\text{O}$  at 100° (Pommerehne, Arch. Pharm. 1898, 236, 105); the picrate forms a yellow crystalline precipitate, decomposing in aqueous solution; the nitrate is unstable. (3) Double salts: with mercuric chloride, colourless prisms, melting with partial decomposition; the aurochloride



orange-yellow needles, m.p. 227°–228°; the platinumchloride  $(\text{C}_7\text{H}_7\text{N}_4\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ , orange crystals belonging to the anorthic system (Pommerehne, *l.c.*; Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 24, 364).

**Derivatives.** 8-Chloroparaxanthine, m.p. 295° (corr.), soluble in 170 parts of hot water, crystallises in prisms; the sodium salt is sparingly, the potassium salt more readily soluble (Fischer and Clemm, Ber. 1898, 31, 2622); it reacts with amines to form the corresponding amino compound, and the ammonia, mono- and di-methylamine and aniline are described (Fischer and Clemm, *ibid.* 1901, 34, 156901).  $\text{C}_7\text{H}_7\text{ON}_4 \cdot \text{H}_2\text{O}$ , obtained by the electrolytic reduction of paraxanthine, decomposes at 250° (Tafel and Dodt, Ber. 1907, 40, 3752), and is readily hydrolysed on heating with hydrochloric acid forming

alone hydrochloride



(Tafel and Mayer, *ibid.* 1908, 41, 2546).

M. A. W.

**PARCHMENT.** *Parchemin* (Fr.); *Pergament* (Ger.). This writing material has been known since the earliest times, but is now made in a manner very superior to that by which it was anciently prepared, as we may judge by inspection of the old vellum and parchment manuscripts. The art of making parchment consists in certain manipulations necessary to prepare the skins of animals of such thinness, flexibility, and firmness as may be required for the different uses to which this substance is applied. Though the skins of all animals may be converted into writing materials, only those of the sheep or the she-goat are used for parchment; those of calves, kids, and still-born lambs for vellum; those of the he-goat, she-goat, and wolves for drum-heads; and those of the ass for battledores. All these skins are treated in the same way, with slight variations, which need no particular detail.

They are first of all prepared by the leather-dresser. After they are taken out of the lime-pit, shaved, and well washed, they must be set to dry in such a way as to prevent their puckering and to render them easily worked. The small manufacturers make use of hoops for this purpose, but on the larger scale a *herse* or stout

wooden frame is employed. This is formed of two uprights and two cross-bars solidly joined together by tenons and mortices so as to form a strong piece of carpentry, which is to be fixed against a wall. These four bars are perforated all over with a series of holes of such dimensions as to receive slightly-tapered boxwood pins truly turned, or even iron bolts. Each of these pins is transferred with a hole like the pin of a violin, by means of which the strings employed in stretching the skin may be tightened. Above the *herse* a shelf is placed for receiving the tools which the workman needs to have always at hand. In order to stretch the skin upon the frame, larger or smaller skewers are employed, according as a greater or smaller piece of it is to be laid hold of. Six holes are made in a straight line to receive the larger, and four to receive the smaller skewers or pins. These small slits are made with a tool like a carpenter's chisel, and of the exact size to admit the skewer. The string round the skewer is affixed to one of the bolts in the frame, which are turned round by means of a key like that by which pianos and harps are tuned. The skewer is threaded through the skin in a state of tension.

Everything being thus prepared, and the skin being well softened, the workman stretches it powerfully by means of the skewers; he attaches the cords to the skewers, and fixes their ends to the iron pegs or pins. He then stretches the skin, first with his hand applied to the pins, and afterwards with the key. Great care must be taken that no wrinkles are formed. The skin is usually stretched more in length than in breadth, from the custom of the trade, though extension in breadth would be preferable, in order to reduce the thickness of the part opposite the backbone.

The workman now resorts to the *herse*. It is a semicircular, double-edged tool, in a double wooden handle. Other forms of the fleshing-knife edge are also used. They are sharpened by a steel. The workman holds the tool in his two hands so as to place the edge perpendicularly to the skin, and, pressing it carefully from above downwards, removes the fleshy excrescences and lays them aside for making glue. He now turns round the *herse* upon the wall, in order to get access to the outside of the skin and to scrape it with the tool inverted, so as to run no risk of cutting the epidermis. He thus removes any adhering filth, and squeezes out some water. The skin must next be ground. For this purpose it is sprinkled upon the fleshy side with sifted chalk or slaked lime, and then rubbed in all directions with a piece of pumice-stone, 4 or 5 inches in area, previously flattened upon a sandstone. The lime soon gets moist from the water contained in the skin. The pumice-stone is then rubbed over the other side of the skin, but without chalk or lime. This operation is necessary only for the best parchment or vellum. The skin is now allowed to dry upon the frame, being carefully protected from sunshine and from frost. In the arid weather of summer a moist cloth needs to be applied to it from time to time, to prevent its drying too suddenly, immediately after which the skewers require to be tightened.

When it is perfectly dry, the white colour is to be removed by rubbing it with the woolly side

of a lambskin. But great care must be taken not to fray the surface—a circumstance of which some manufacturers are so much afraid as not to use either chalk or lime in the polishing. Should any grease be detected upon it, it must be removed by steeping it in a lime-pit for 10 days, then stretching it anew upon the *herse*, after which it is transferred to the *scraper*.

This workman employs here an edge tool of the same shape as the fleshing-knife, but larger and sharper. He mounts the skin upon a frame like the *herse* above described; but he extends it merely with cords, without skewers or pins, and supports it generally upon a piece of raw calfskin strongly stretched. The tail of the skin being placed towards the bottom of the frame, the workman first pares off with a sharp knife any considerable roughnesses, and then scrapes the outside surface obliquely downwards with the proper tools till it becomes perfectly smooth; the fleshy side needs no such operation; and indeed, were both sides scraped, the skin would be apt to become too thin, the only object of the scraper being to equalise its thickness. Whatever irregularities remain may be removed with a piece of the finest pumice-stone well flattened beforehand upon a fine sandstone. This process is performed by laying the rough parchment upon an oblong plank of wood in the form of a stool, the plank being covered with a piece of soft parchment stuffed with wool, to form an elastic cushion for the grinding operation. It is merely the outside surface that requires to be pumiced. The celebrated Strasburg vellum is prepared with remarkably fine pumice-stone. If any small holes happen to be made in the parchment they must be neatly patched by cutting their edges thin and pasting on small pieces with gum-water.

Another method of finishing the skin is to subject it, after a final scalding, to a bath of lime-water, and then powder it on both sides with French chalk, the excess of which is brushed off when dry. The skin is afterwards wiped over with a wet sponge and, when again dry, is rubbed over with a piece of flannel (Brand, Eng. Pat. 11693, 1893). Treatment with a bath of alum solution is said to prevent the ink soaking in and to make the parchment easier to use (Brand, *ibid.* 14384, 1894).

Parchment is coloured green only. The following is the process. In 500 parts of rain-water boil 8 of cream-of-tartar and 30 of crystallised verdigris; when this solution is cold pour into it 4 parts of nitric acid. Moisten the parchment with a brush, and then apply the above liquid evenly over its surface. Lastly, the necessary lustre may be given with white-of-egg and a solution of gum arabic (Ure).

**PARCHMENT PAPER** (*vegetable parchment*) is a modified form of paper, resembling parchment, produced by the action of sulphuric acid, zinc chloride solution or cuprammonium solutions on ordinary paper.

*Manufacture by the sulphuric acid process.*—The sulphuric acid used should have a density of 59°–60°B., and may be prepared by mixing 1 vol. of water with 2 vols. of ordinary strong sulphuric acid of 66°B. It is important that the temperature should not exceed 16°C. (Lotter, J. Soc. Chem. Ind. 1895, 59). The paper may contain linen or cotton fibres, or both, but

regard must be had to the fact that linen is not parchmentised as quickly as cotton. The original paper also affects the product in that a more porous paper absorbs the acid more readily and is more completely parchmentised and, therefore, more transparent. Because it is important for the acid to penetrate the fibre thick papers cannot be parchmentised, and thick vegetable parchment is made by pressing together two, three, or more sheets of thinner paper as they leave the acid bath. After they have been washed and dried it is found that they have become perfectly united.

In the hand process the operator, wearing rubber gloves, dips the sheets of paper into the acid bath for the requisite time (2-15 seconds, according to the nature of the paper and of the product desired), and then throws them into a bath of water, from which they are passed through other wash-waters, one of which contains a small proportion of ammonia. After a final wash the sheets are dried under pressure.

In the continuous process, a band of paper passes from a roll and under glass or lead rollers in the stoneware or lead tank containing the acid at such a rate that it is immersed for the time that previous experiment has shown to be necessary for its conversion into parchment. As it leaves the bath, it passes between rubber rollers, by which the excess of acid is removed and returned to the bath, and then goes through various washing tanks, one of which contains a dilute solution of ammonia. The washing is made more complete by spraying the paper with water (see Arnold, Eng. Pat. 8130, 1885; J. Soc. Chem. Ind. 1885, 609). After washing, the parchment is dried by passage over heated, felt-covered rollers, and is finally calendered in the same way as ordinary papers (J. Soc. Chem. Ind. 1894, 414; see also Wilbaux, Eng. Pat. 17268, 1890; J. Soc. Chem. Ind. 1891, 566).

\* Parchment paper is sometimes rather brittle when dry, and this is overcome by impregnating it with hygroscopic substances like calcium and magnesium chlorides and glycerol (Eichorn, Eng. Pat. 885; J. Soc. Chem. Ind. 1885, 609). P. B. has patented a continuous process in which the paper, before drying, passes through a bath of glycerol (Eng. Pat. 8473, 1892; J. Soc. Chem. Ind. 1892, 935).

Vegetable parchment may be made white and opaque and repellent to water by adding to the acid-bath white opaque pigments, e.g. barium sulphate, and water-repellent substances, like mineral oils (Sachsenröder, Fr. Pat. 362463, 1906; J. Soc. Chem. Ind. 1906, 713).

**Manufacture by zinc chloride and cuprammonium methods.** The preparation of parchment-paper by the action of a very strong solution of zinc chloride upon ordinary paper differs little from the above method, except that a longer time is required for the action, and the alkali bath is omitted from the washing.

Cuprammonium solutions (v. COPPER) gelatinise paper in a similar way and when the product is dried by steam-heat it is green, owing to the presence in it of copper.

**Properties and uses.**—The action of sulphuric acid in parchmentising paper is to convert the superficial layers of cellulose into a gelatinous mass which fills up the interstices between the fibres of the paper and renders it practically

impervious to gases and liquids. During this change the paper shrinks 10-30 p.c. in area and up to 30 p.c. in thickness, and shows a corresponding increase in sp.gr. of 30-40 p.c. At the same time its strength is increased three- or fourfold and the product has about three-quarters the strength of animal parchment of the same thickness.

Good parchment paper is unaffected even by repeated soaking in boiling water and drying, and can thus be distinguished from various imitation parchment papers which are made by coating ordinary paper with size, albumin, blood serum, &c., with or without added colouring matter, and are at once disintegrated by hot water. In addition to being waterproof and gas-tight, it is unaffected by cold acids and by caustic alkalis; prolonged action of hot conc. hydrochloric acid, however, converts it into dextrin.

It is not liable to mould when damp and resists the attacks of insects, and thus possesses certain advantages over animal parchment. It takes dyes well.

It readily absorbs printers' ink and writing ink, and these cannot afterwards be erased without serious injury to the parchment. On this account it is much used for the preparation of important documents.

Vegetable parchment is also used for wrapping tobacco, &c., for luting the joints of stills, for covering jars containing preserves, &c., and for paper-bags for cooking and steaming food. It has been manufactured and used for electrical insulation (London and Bailey, Eng. Pat. 12711, 1895; see also L. E. Andés, The Treatment of Paper for Special Purposes).

**PARIGENIN and PARIGLIN** v. SARSAPARILLA.

**PARILLIN** v. GLUCOSIDES.

**PARILLINIC ACID** v. SARSAPARILLA.

**PARIS BLUE.** This term is occasionally applied to Prussian blue, and also to the products obtained by heating aniline with stannic chloride.

**PARIS GREEN.** An aceto-arsenite of copper used as a pigment, and occasionally as an insecticide on plants.

**PARIS LAKE.** *Carmine lake* v. LAKES.

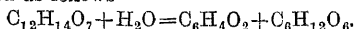
**PARIS RED.** A variety of rouge employed for polishing.

**PARIS WHITE.** *Whiting* v. PAINTS.

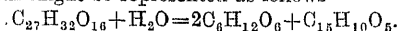
**PARIS YELLOW.** *Normal lead chromate* v. CHROMIUM.

**PARSLEY.** *Apiin*, the glucoside of apigenin, is found in the leaves, stem, and seeds of parsley (*Carum* [*Apium*] *Petroselinum* [Benth. and Hook]) (Rump, Bechner's Repert. f. Pharm. 1836, 6, 6; Braconnot, Ann. Chim. Phys. 1843 (iii.) 9, 250). Both authors obtained it in mass by extracting parsley seeds with water, and considering the mass which it gelatinised, Braconnot included it among the members of the pectin class. Subsequently, Planta and Wallace assigned to it the formula  $C_{24}H_{25}O_{13}$  (Annalen, 1850, 74, 262), and though by the action of boiling dilute acids a brown substance,  $C_{24}H_{20}O_9$ , was produced, it did not appear that apiin was a glucoside. On the other hand, Lindenhorn (Inaugural Dissert. Würzburg, 1867), who obtained this substance in a crystalline

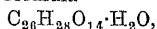
condition, found that by the action of dilute acids it was decomposed into glucose and apigenin, and that the reaction probably proceeded as follows



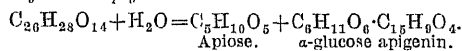
Von Gerichten (Ber. 1876, 9, 1124), who found for apiin and apigenin numbers identical with those given by Lindenhorn, showed that on fusion with alkali apiin gave *phloroglucinol* and an acid not closely examined, but which, by the further action of the alkali, gave *protocatechuic acid* besides some *oxalic*, *formic*, and *para-hydroxybenzoic acids*. As a result of his investigation, von Gerichten considered the most probable formula for apigenin to be  $C_{15}H_{10}O_5$ , and that the decomposition of the glucoside apiin with acids might be represented as follows—



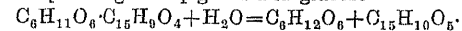
In a later communication (Annalen, 318, 124), he adopted the formula



and found that on hydrolysing apiin with  $\frac{1}{2}$  p.c. sulphuric acid it is converted into *apiose* and  *$\alpha$ -glucose apigenin*

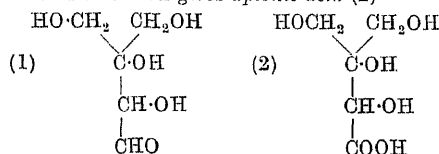


By the prolonged action of the acid, the latter compound gives apigenin and glucose



Apiin therefore contains a disaccharose nucleus which on hydrolysis yields dextrose and apiose.

*Apiose* is an aldopentose of the formula (1) and on oxidation gives *apionic acid* (2)



By the action of hydriodic acid and phosphorus *apionic acid* is reduced to *iso-valeric acid*.

When apiin is boiled with nitric acid in 60 p.c. acetic acid it is converted into the nitromonoglucoside, *nitroapigetrin*  $C_{21}H_{21}O_{11}NO_2$ , a yellow crystalline powder, m.p.  $254^\circ$ – $255^\circ$ , soluble in alkaline solutions with a yellow colour (Perkin, Chem. Soc. Trans. 1900, 416, 77).

*Apiin* consists of colourless needles, m.p.  $228^\circ$ , easily soluble in hot water and alcohol. From these solutions it separates on cooling in the gelatinous condition.

Whereas apiin can be most readily obtained in a pure condition from the seeds of parsley, it has been shown by von Gerichten that the stem and leaves of this plant contain in addition a glucoside of a *luteolin monomethylether*. By fusion with alkali, pure apigenin gives *phloroglucinol* and *p-hydroxybenzoic acid* (Ber. 1900, 33, 2334). The previous isolation of *protocatechuic acid*, according to this method by von Gerichten, and Perkin (Chem. Soc. Trans. 1897, 71, 805) was due to its contamination with a trace of the luteolin derivative.

In order to prepare apigenin, Perkin (l.c.) fused a mixture of apiin for 20 hours with 3 litres of concentrated sulphuric acid (sp.gr. 1.04). The crude colouring matter is extracted with boiling alcohol, and the extract treated with alcoholic

lead acetate solution, drop by drop, until the supernatant liquid becomes colourless. The lead precipitate is then removed, and the filtrate after treatment with a few drops of acetic acid is evaporated to a small bulk. By addition of a little boiling water and gentle evaporation, the apigenin separates in a crystalline condition.

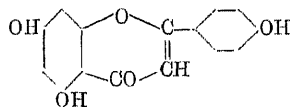
Should the substance be contaminated with luteolin monomethylether, it is digested for 2 hours with boiling concentrated sulphuric acid (sp.gr. 1.96) and the product extracted with alcohol. The more soluble luteolin thus formed remains in solution (Czajkowski, v. Kostanecki and Tambor, Ber. 1900, 33, 1996).

Apigenin crystallises in almost colourless needles, and dissolves in alkaline solutions with a yellow colouration. By means of acetic anhydride *triacetyl apigenin*, colourless needles, m.p.  $181^\circ$ – $182^\circ$ , is produced (C., K. and T.), but when methylated by means of methyl iodide, only a *dimethylether*

$C_{15}H_8O_3(OCH_3)_2$ , pale yellow needles, m.p.  $171^\circ$ – $172^\circ$  (Perkin, l.c.), is formed. *Triacetyl apigenin* yields

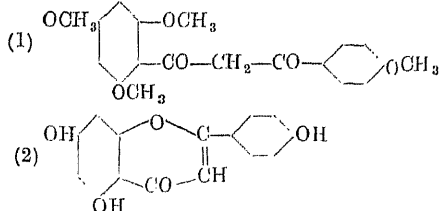
needles, m.p.  $195^\circ$ – $196^\circ$  (P.), and by means of alcoholic potash is transformed into a yellow potassium salt which is decomposed by washing with water. When hydrolysed with alcoholic potash, apigenin dimethylether yields *anisic acid* and a syrupy phenolic substance which probably is *resorcinol*.

If a mixture of apigenin and *hydroxychrysin* is subjected to hydroxylation (Perkin, l.c.), the product is a mixture of *hydroxychrysin* and *trihydroxyflavone*. Perkin assigned to apigenin the constitution of an *hydroxychrysin*, or 1:3:4':*trihydroxyflavone*



Somewhat later, Czajkowski, v. Kostanecki and Tambor (l.c.) synthesised apigenin by a series of reactions similar to those employed for the preparation of *chrysin* (Emilewicz, v. Kostanecki, Ber. 32, 2448).

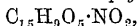
*Phloracetophenone trimethylether* condensed with *ethyl anisate* in the presence of sodium gives *triethyl apigenin* (1), and this on treatment with alkali is converted into apigenin (2).



The following derivatives of apigenin have been prepared.

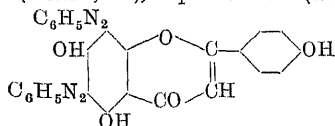
*Apigenin diethylether*,  $C_{15}H_{12}O_3(OC_2H_5)_2$ , yellow needles, m.p.  $161^\circ$ – $162^\circ$  (P.),  $163^\circ$ – $164^\circ$  (C., K. and T.); *acetyl apigenin diethylether*,  $C_{15}H_{12}O_3(OC_2H_5)_2 \cdot C_2H_3O$

colourless needles, m.p. 151°–152° (P.), 148°–149.5° (C., K. and T.); *tribenzoylapigenin*  $C_{15}H_7O_5(C_7H_5O)_3$ , colourless needles, m.p. 210°–212° (F.); *tribromapigenin*  $C_{15}H_5Br_3O_5$ , pale yellow needles; *mononitroapigenin*



orange yellow prismatic needles; *trinitroapigenin*  $C_{15}H_7O_5(NO_2)_3$ , minute yellow needles; and *tetranitroapigenin*  $C_{15}H_5O_5(NO_2)_4$ , almost colourless needles, m.p. 243°–244° (decomp.).

*Disazobenzene apigenin* crystallises in red needles (Perkin, l.c.), m.p. 290°–292° (decomp.)



and with acetic anhydride gives only the *monoacetyl-derivative*  $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$ , orange red needles which commence to decompose at 260° and melt at about 277°–280°.

Apigenin closely resembles chrysin in its tinctorial properties, although it is a somewhat stronger dyestuff. The shades it gives upon wool mordanted with aluminium, chromium, and iron are respectively pure yellow, weak yellow orange, and chocolate brown.

Apigenin is also present in weld (*Reseda luteola*) (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1314), and exists probably also in camomile flowers (Perkin) (private communication). A. G. P.

#### PARSLEY, OIL OF, v. OILS, ESSENTIAL.

**PARSNIP**, *Peucedanum sativum* (Benth. and Hook.). The tap root is used as a vegetable. König gives as the average composition—

Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash
83.2	1.4	0.4	2.3	8.1	3.6	1.0

It has also been used as a root crop for the feeding of horses, cows, and bullocks. The yield is from 12 to 24 tons per acre, and the material possesses higher feeding value than turnips, mangolds, or carrots (Guépin, Ann. Agron. 1900, 26, 476). The ash is rich in potash (42 p.c.). H. I.

**PARTING**. The separation of gold and silver by means of nitric acid, v. ASSAYING.

**PARTINIUM**. An alloy of aluminium and tungsten used in automobile construction.

#### PASTES v. GEMS, IMITATION.

**PATCHOULI CAMPHOR** v. CAMPHORS; also OILS, ESSENTIAL.

#### PATCHOULI OIL v. OILS, ESSENTIAL.

#### PATENT LEATHER VARNISH v. VARNISH.

**PATENT PHOSPHINES** v. ACRIDINE DYE-STUFFS.

#### PATERAITE v. MOLYBDENUM.

**PATINA**. The green film which forms upon bronze and copper mouldings, and consisting of basic copper carbonate. On bronze statues it produces a pleasing effect owing to its colour, smoothness, and transparency, so that the bronze itself may be seen through it in places. The conditions which favour the formation of patina are a pure atmosphere, the presence of moisture in the air or in the earth where the articles may have lain buried, and a smooth surface. The finest examples of patina are found upon bronzes of ancient manufacture in

which much tin and little zinc was used as alloy. The effect of a natural, and consequently slowly formed, coating of patina is frequently imitated artificially by wetting articles of bronze with dilute acids.

**PATRONITE**. A vanadium sulphide ( $VS_4$  or  $V_2S_5 + nS$ ), forming a large deposit in the Quisque (or Minasragra) district, near Cerro de Pasco in Peru. It is amorphous and dull with a black or very dark greenish-black colour, and somewhat resembles asphaltum in appearance. Analyses show 15 to 24.8 p.c. of vanadium with combined sulphur and various impurities (silica, alumina, free sulphur, carbonaceous matter, &c.). Sp.gr. 2.65–2.71. Banded with vanadiferous asphaltum, *quisquite* (q.v.), and a coke-like material, it forms a large vein or lenticular mass in red shales of Cretaceous age which are penetrated by dykes of igneous rock. This deposit has been extensively mined; the material is roasted to drive off volatile constituents, and the residue exported for the manufacture of vanadium steel. (See W. F. Hillebrand, Amer. J. Sci. 1907, xxiv, 141; D. F. Hewett, Trans. Amer. Inst. Mining Engin. 1910, xl (1909), 274) (v. VANADIUM). L. J. S.

#### PAULLINITANNIC ACID v. GUARANA.

#### PAVIN v. HORSE CHESTNUT.

**PAWPAW**, *Carica Papaya* (Linn.). The fruit is edible. According to Prinsen Geerligs (Chem. Zeit. 1897, 21, 719), the following figures give its average constitution:—

Average wt. of 1 fruit	Flesh	Rind	Seeds
600 grammes	65	10	25 p.c.

The flesh contains—glucose, 2.6 p.c.; fructose, 2.1 p.c.; cane sugar, 0.9 p.c.

Of more importance is the occurrence in the juice of the fruit, of an enzyme—*papayin* or *papain*—which resembles pepsin. In the West Indies this juice is collected by making incisions in the fruit while still on the tree, with a bone or wooden knife, and receiving the juice in earthen or glass vessels. The juice, which rapidly coagulates to a white curd, is very putrescible, and has therefore to be rapidly dried, either in the sun or by artificial heat, care being taken not to raise the temperature much above 35°–40° (v. PAPAIN). H. I.

**PEA**. The garden pea, *Pisum sativum* (Linn.), is a leguminous plant, growing in temperate climates. The seeds are used largely as human food in the green immature condition and also when ripe and dry.

The air-dried ripe seeds, on the average, contain (König)—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
13.6	23.4	1.9	52.7	5.6	2.8

Of the total nitrogen in peas, non-proteid nitrogen constitutes from 8 to 11.5 p.c. The proteids have been investigated by Osborne and Campbell (J. Amer. Chem. Soc. 1896, 18, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 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1830, 1831, 1832, 1833, 1834, 1835,



legumelin is an albumin, coagulates below 80° and resembles the leucosin of wheat (Osborne and Harris, J. Biol. Chem. 1907, 3, 213). For description of the hydrolysis of these proteids, v. Osborne and Heyl J. Biol. Chem. 1908, 5, 187.

Choline and trigonelline have been found in peas (Schulze and Frankfurt, Ber. 1894, 27, 769).

The nitrogen-free extract contains about 68 p.c. of starch, 10.5 p.c. of dextrine, &c., and 4 p.c. of pentosans. The fat is a pale-yellow oil, containing much lecithin and some phyto-sterol.

Green peas—the unripe form in which the seeds are usually eaten as a vegetable, contain on the average—

Water	Protein	Fat	Sugar and other N-free subst.	Crude fibre	Ash
77.7	6.6	0.5	12.4	1.9	0.9

The nitrogenous matter consists largely of non-proteid bodies, 25–33 p.c. of the total nitrogen being in this form.

The ash of peas contains—

K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
41.8	1.0	5.0	8.0	0.9	36.4	3.5	0.9	1.5

Bottled and canned green peas are largely prepared, and in many cases the colour is rendered brighter by the use of copper compounds, added either by actual addition of some copper salt or by boiling the peas in a solution of copper sulphate.

For the treatment of peas by copper, see p. 104. In treatment; 50 milligrams of copper per kilogramme of peas is said to be sufficient to impart a permanent and adequate greenness to peas, and twice this amount is permitted by law in France and Italy (Wynter Blyth). Such addition of copper is illegal in England.

The field pea, *Pisum arvense*, is an important farm crop, the seed furnishing an excellent and richly nitrogenous food for fattening stock, while the power of collecting nitrogen from the air, which peas in common with other *leguminosae* possess, serves to enrich the soil on which it is grown.

The following analyses by Kellner show the average composition of field peas :—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Green plant, flowering	84.6	4.0	0.5	5.1	4.5	1.4
Hay, cut in flower	16.7	14.3	2.6	34.2	25.2	7.0
Straw, cut when ripe	13.6	9.0	1.6	33.7	35.5	6.6
Seeds, air-dried	14.0	22.5	1.6	53.7	5.4	2.8
Husks	12.0	7.3	1.2	31.9	44.7	2.9
Bran	11.7	16.8	1.7	46.2	20.1	3.5
Feeding meal	13.5	23.4	2.0	51.0	7.0	3.1

H. I.

#### PEA IRON ORE v. IRON.

#### PEA-NUT, Earth-nut or Ground-nut,

*Arachis hypogaea* (L.). The seed of a plant growing underground. After flowering, the stalk bends over and enters the soil, where the seeds grow and ripen. The seeds are contained in paper-like pods, or husks, and there are usually two, though in some varieties four seeds in each pod.

The average composition of the shelled seed is given by König as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
17.5	27.5	44.5	15.7	2.4	2.5

The writer has found in samples of Transvaal pea-nuts considerably higher proportions

of oil, e.g. the following three analyses may be quoted (A grown in the Transvaal from Virginian seed; B grown in the Transvaal from Spanish seed; C import from 'Mammoth') :—

100 pods of A weighed 102.4 grammes and contained 170 kernels;	
100 pods of B weighed 102.4 grammes and contained 170 kernels;	
100 pods of C weighed 190.3 grammes and contained 288 kernels.	

A consisted of 66 p.c. kernel, B of 76.4 p.c., and C of 71.7 p.c. kernel.

The kernels, on analysis, gave the following :—

	A	B	C
Moisture	4.88	5.05	4.37 p.c.
Protein	30.13	31.19	24.82 „
Oil	46.06	46.08	54.35 „

The seeds, after roasting, possess an agreeable nutty flavour, and are used to some extent as human food. They are of more importance as a source of oil (*v. Arachis oil*, Art. OILS, FIXED, AND FATS), while the press cake left is a valuable cattle food containing, according to Kellner—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
9.8	44.5	9.2	23.8	5.2	7.5

Samples containing up to 50 p.c. protein are not uncommon, and, if the seeds are free from sand, the ash is lower than the figures given.

The 'vines,' after removal of the seed, may be used as hay for cattle. American analyses show them to contain—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
10.0	10.0	3.6	42.0	22.0	12.4

For a description of the cultivation and applications of the pea-nut or 'pindars' in Jamaica, see J. Imp. Inst. 1898, Dec. 341.

H. I.

**PEACH, *Prunus Persica* (Stokes),** a tree growing in warm climates, bearing a fruit which is valued for table purposes. Many varieties are known; they may be divided into two types—cling-stone and free-stone peaches, according to the character of the connection between the flesh and the stone or 'pit' of the fruit.

König gives as the average composition—

	Free Invert	Cane sugar	Other N-free ext.	Fibre	Ash
Water	82.0	0.9	0.7	3.7	4.5
Protein	1.2	6.5	0.6		

Under 'fibre' in the above figures is included the stone, which constitutes from 4.6 to 6.8 p.c. of the whole fruit. About 0.8 p.c. of amygdalin is present. The peach kernel contains oil, amygdalin, and a proteid, *amandin* (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 609). For changes in composition during ripening, v. Bigelow and Gore (J. Amer. Chem. Soc. 1905, 27, 915).

The juice of peaches has a sp.gr. of about 1.05, contains 13 p.c. of total solids, including 2 p.c. invert sugar, 7 p.c. of cane sugar, and 0.6 p.c. free acid (as malic acid). It can readily be fermented, and is used as a source of alcohol—so-called peach brandy.

Peaches are often preserved by drying, or canning in syrup. American analyses of canned peaches show them to contain—

Water	Protein	Fat	N-free extract	fibre	Ash
88.1	0.7	0.1	10.8		0.3

H. I.

**PEACH KERNEL, OIL OF, v. OILS,** ESSENTIAL; also OILS, FIXED, AND FATS.

**PEACH WOOD v. BEAZL WOOD.**

**PEACOCK-COPPER ORE v. COPPER-PYRITES.**

**PEAR, *Pyrus communis* (Linn.).** Many varieties are known. The average composition of the ripe fruit is given by König as—

	Free Invert Cane	Other N- Fibre and
Water	83.8	3.4
Protein	0.4	2.8
acid sugar	0.2	0.3
free extract	7.1	1.5
skins	1.5	3.4
Ash	0.3	0.3

A considerable quantity of pectin and pectous substances is present. Pear juice, like apple juice, readily ferments and yields an alcoholic liquid—perry—resembling cider. From this a brandy can be prepared (*v. Windisch, Zeit. Spiritusind.* 1905, 2887). Tannin is present, especially in the rind (Kehlhofer, *Bied. Zentr.* 1900, 29, 248). The rind also contains a wax melting at 68° (Seifert, *Landw. Versuchs. Stat.* 1894, 45, 29). The dried seeds of pears were examined by Huber (*Landw. Versuchs. Stat.* 1911, 75, 443), who found them to contain—

	Fat	Sugar	Furfurals	Crude fibre	Protein	Amides	Ash
	25.0	5.4	6.7	9.0	5.4	0.2	3.8

The leaves of pear trees contain from 1.2 to 1.4 p.c. of a glucoside (m.p. 194°), which, on hydrolysis, yields quinol, and is probably identical with arbutin (Bourquelot and Fichtenholz, *Compt. rend.* 1910, 151, 81). The existence of quinol in the buds of peartrees was observed by Rivière and Bailhache (*Compt. rend.* 1904, 139, 81).

The ash of pears (whole fruit) was found by Wolff to contain—

K <sub>2</sub> O	Na <sub>2</sub> O	MgO	CaO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>
54.7	8.5	5.2	8.0	15.3	5.7	1.5

Pears are sometimes dried, but more generally preserved by canning. American analyses give the following:—

	Water	Protein	Fat	Total carbo-	Ash
				hydrates	
Dried pears	16.5	2.8	2.4	72.9	2.4
Canned pears	81.1	0.3	0.3	18.0	0.3

H. I.

**PEARCEITE v. POLYBASITE.**

**PEARL ASH.** A variety of potassium carbonate, *v. POTASSIUM.*

**PEARL SINTER.** A kind of opal found in the cavities of volcanic tufa.

**PEARL SPAR v. DOLOMITE.**

**PEARL WHITE** is (1) a basic bismuth nitrate or oxychloride (*v. BISMUTH*); (2) a preparation of mother-of-pearl.

**PEARL-HARDENING (*Satin spar* or *Anna-line*)** is the trade name for artificial crystallised calcium sulphate. It may be prepared by treating calcium chloride solution with dilute sulphuric acid; by boiling waste gypsum with hydrochloric acid (*Eng. Pat.* 1577, 1897) or by the double decomposition of sodium or magnesium sulphate with calcium chloride (*Eng. Pat.* 7797, 1891). It is used in paper manufacture as a filling for writing paper (*v. CALCIUM*).

**PEARLITE.** The name given by Sorby (*J. Iron and Steel Inst.* 1886, 140; 1887, 255) to the eutectic mixture of ferrite and cementite present in steels. It may consist of alternate lamellæ of the constituents, which in oblique light show iridescent colours like mother-of-pearl, or it may exist in granular or 'beady' forms (*Benedicks, Métallurgie*, 1909, 6, 567). The two constituents are identical with 'free'

ferrite and cementite (Ledebur, *Stahl. u. Eisen*, 1887, 8, 742; 1891, 11, 294).

It is the principal, sometimes the only constituent of intermediate steels and under the microscope is characterised by polishing in relief or etching, when the cementite stands out from the softer ferrite.

**PEARLS.** Calcareous concretions formed by various molluscs, those used in jewellery being mostly obtained from the large pearl-oyster, *Avicula (*Meleagrina*) margaritifera* (Lam.). The analysis of several fine white pearls by Harley gave calcium carbonate, 91.72; organic matter, 5.94; water, 2.23 (*Proc. Roy. Soc.* 1889, 43, 461). The calcium carbonate is of the orthorhombic modification identical with the mineral aragonite, and the organic matter is chiefly conchiolin. The sp. gr. of pearls varies between 2.650 and 2.686. Most pearls present a concentric structure, having been formed by successive deposits around a nucleus, which may be a grain of sand, a parasitic organism, a fragment of seaweed, or some other foreign body which by irritating the mollusc stimulates the secretion of nacre. The pearls are usually found in the mantle, but sometimes in the muscles of the mollusc; or, having escaped from the tissues, they may become adherent to the shell. To be valued by the jeweller, the pearl should be of spherical form, while its skin or outer coat should display the delicate iridescent sheen known as the 'orient.' Pearls of more or less hemispherical shape, cut from the shell, are termed *boutons*; while those which are warty or irregular in form pass under the name of *baroque*. Occasionally the pearl is found completely embedded in the mother-of-pearl. Some pearls, instead of showing a concentric structure, are crystalline, being composed of striated prisms radiating from the centre, and these may or may not possess a nucleus (Harley, *Proc. Roy. Soc.* 1889, xlv, 612).

The principal pearl fisheries are those of Torres Straits and the north-west coast of Western Australia, the Sulu Archipelago, Ceylon, and the coast of Madras, the Philippines, and the Gambier and Pomotou Islands. The American fisheries are chiefly in the Caribbean Sea, off the coast of California, and near Panama. The pearls are mostly derived from *Meleagrina Californica* (W. H. Dall, *Americ. Nat.* 1883, 17, 579, 731; E. W. Streeter, *Pearls and Pearlaring Life*, London, 1886).

Coloured pearls are occasionally found, the tint in each case being dependent on that of the nacre lining the shell. The highly-prized black pearls are obtained chiefly from Mexico, and it has been suggested that the colour is due to the presence in the water of salts of silver, derived from silver mines. Pearls have been obtained by means of silver salts. Pink pearls, sometimes finely water-lined, are mostly derived from the conch shell *Strombus gigas*; while large, coarse, yellowish pearls are obtained from the great clam, *Tridacna gigas*.

The principal source of fresh-water pearls is the pearl-mussel (*Unio margaritifera*), a mollusc widely distributed in the rivers of northern temperate regions. It is found in the Tay, Forth, Earn, Doon, and many other mountain streams in Scotland. Scottish pearl-fishing was

revived in 1860, and successfully carried on for some years by M. Unger. The pearl-mussel is also found in Cumberland; in Wales, especially in the Conway; and in Ireland. On the Continent pearl-fishing has been carried on in Bohemia, and Bavaria; and even in Lapland. The American rivers also produce pearls, especially in New York, Ohio, and in Canada. Pearls of N. America, New York, (1890). Fresh-water pearls are likewise obtained from China and Japan, and the Chinese exhibit much skill in inducing the formation of pearl by the artificial introduction of certain objects, upon which the mollusc deposits a nacreous layer. Chinese shells with images of Buddha formed of pearl adherent to the inner surface are well known to collectors (Maogowan, Journ. Soc. Arts, 1853, ii. 72).

The so-called cocoa-nut pearls, from the Malay Archipelago, are pearl-like bodies, resembling ivory, said to be found inside cocoanuts. Certain bodies which have been described as mammalian pearls are simply biliary concretions, formed mainly of cholesterol.

Artificial pearls are manufactured on the Continent in a variety of ways. Some are globes of thin opaline glass, filled with gum or wax, and deadened on the surface by means of hydrofluoric acid. The better kinds are glass globules lined with a nacreous composition, formed by digesting the silvery scales of the bleak in ammonia. Roman pearls are glass spheres, to which the nacreous material is applied externally. Celluloid, incorporated with fish scales, has become a favourite material for artificial pearls. Black pearls have been imitated by beads of a very compact hæmatite, which may be polished so as to present a kind of iridescent lustre. Pink pearls are frequently

made of pale coral (*v.* MOTHER-OF-PEARL); Herdman and Hornell, Rep. Ceylon Pearl Fisheries (Roy. Soc. London, 1903); (J. F. Kunz and C. H. Stevenson, The Book of the Pearl (New York, 1908).

F. W. R.

**PEAT and TURF** *v.* FUEL.

**PEATWAX** *v.* WAXES.

**PELARGONIC ACID** *v.* NONOIC ACIDS.

**PELLETIERINE** *v.* VEGETO-ALKALOIDS.

**PELLITORY RESIN** *v.* RESINS.

**PENNETTIER'S GREEN**. *Hydrated chromium sesquioxide v.* CHROMIUM.

**PENNYROYAL, OIL OF,** *v.* OILS, ESSENTIAL.

**PENTADECATOIC ACID**  $C_{14}H_{28}COOH$ , m.p.  $51^{\circ}$ , b.p.  $257^{\circ}$  (100 m.m.), is obtained by the oxidation of methylpentadecylketone (Kraft, Ber. 1879, 1871) and by heating pentadecyl alcohol with potassium carbonate (Panics, Monatsh. 15, 14).

**PENTAHYDROXYBENZENE** *v.* PHENOL AND ITS HOMOLOGUES.

**PENTAL** *v.* SYNTHETIC DRUGS.

**Cyclo-PENTANEDIONE** *v.* KETONES.

**Cyclo-PENTANONE** *v.* KETONES.

**PENTLANDITE**. A native sulphide of nickel (10-40 p.c.) and iron. The N.Y.S. forming granular masses with a pale bluish-grey color. It is an important constituent of the extensively mined nickel ores of Sudbury in Ontario (*v.* PYRRHOTITE); and it has also been found in some

quantity in the Essachossan mine near Inverary in Argyllshire, and at Lillehammer in Norway.

L. J. S.

**PENTOSANS, PENTOSES** *v.* CARBOHYDRATES.

**PEPPER** is the dried fruit of *Piper nigrum* (Linn.), a plant of the same family, *Piperaceæ*, as the Betel pepper and Long pepper.

It is a climbing plant, from 12 to 20 ft. high, growing in the East and West Indies and cultivated in many tropical countries. The fruit is borne on terminal flower stalks, 20 to 30 on each stem, the berries being about 5 mm. in diameter. It is gathered when it begins to turn red, dried in the sun or by artificial heat, after which it becomes black and shrivelled. Two crops are collected annually.

The chief varieties coming into the market at the present time are Mangalore (very little), Malabar, Ceylon, Java, and Tellicherry, Trang, Penang, and Singapore, the first mentioned being the most esteemed in the trade.

*Preparation.* Black pepper is the whole berry gathered in the green condition and dried in the sun or in the case of some varieties, as that of Singapore, over a fire.

White pepper is the same berry, gathered when more mature, but deprived of a portion of the pericarp or outer skin by macerating in water, drying, and then rubbing between the hands, from 6 to 12 p.c. of husks being thus obtained. The berries even after this are larger than those of Black pepper, but in no other respect does the greater degree of ripeness show itself.

*Composition.* The constituents to which the flavour and aroma of pepper are due are a resin, an alkaloid, *piperine*, and a volatile oil. According to W. Johnstone, *piperidine* is also present, but this has been contradicted (Zeitsch. öfentl. Chem. 1904, 10, 137). The usual plant constituents, including much starch, make up the bulk of the material.

The following table shows the comparative composition of the two varieties.

TABLE I.

COMPOSITION OF PEPPER.

(Richardson, U.S. Dept. of Agriculture, Bureau of Chem. Bul. 13, II., 206).

	Black pepper	White pepper
Water . . .	8.0 to 11.0	8.0 to 11.0
Ash . . .	2.75 " 5.0	1.0 " 2.0
Volatile oil . .	0.50 " 1.75	0.5 " 1.75
Piperine and resin	7.0 " 8.0	7.0 " 8.0
Starch . . .	32.0 " 38.0	40.0 " 44.0
Crude fibre . .	8.0 " 11.0	4.11 " 8.0
Albuminoids . .	7.0 " 12.0	8.0 " 10.0

Pepper itself is mainly employed as a condiment, the shells being used for tinned foods, and the *piperine* is *official* in the pharmacopœia, and like the volatile oil acts as a carminative and stomachic.

*Adulteration.* The number of different substances which have been recorded from time to time as adulterants of pepper is very large, but in this country but little sophistication has been detected of recent years.

Excessive proportions of mineral matters may be present, owing to the whole berries having been insufficiently cleansed from adherent earth; or to their having been coated with kaolin, French chalk, or similar material,

so as to enable black pepper to counterfeit the white variety; a high ash may also result from the deliberate addition of mineral substances to the ground pepper.

The commonest adulterant, however, is added starch, that of rice being most frequently employed. Some years back, ground olive stones ('poivrette' or 'pepperette') were frequently met with in samples examined under the Food and Drugs Acts, and many prosecutions resulted. The husk removed from white pepper in the course of manufacture is frequently added to both black and white peppers, being in the latter case bleached. In white pepper it must certainly be regarded as an adulterant if the proportion of added husk is at all substantial, and numerous successes have been recorded. The husk of *Piper longum* was formerly fairly common.

A more objectionable offence arises from the craze for whiteness in pepper, and it is hardly too much to say that, but for this, adulteration would be much less frequent. White pepper is bleached to make it whiter still, and fetches a higher price in consequence although very deficient in aroma. The exact process is kept secret, though it is believed to involve the use of bleaching powder or sulphurous acid. The bleaching process naturally removes much of the aroma and the purchaser pays a higher price for an impoverished product, which is much more likely to become mouldy in consequence of the treatment it has undergone.

Of the rarer adulterants which, however, still appear to be met with in America and elsewhere, may be mentioned spent ginger, mustard hulls, linseed meal, ground almond shells, sawdust and barium sulphate.

**Detection of adulteration.** (1) Microscopical examination. For the detection of added starch the ground sample should be examined in water or dilute glycerol without attempting to reduce the material to a very fine powder. The masses of starch granules, cemented together with protein substances, will then retain the form of the cells in which they were enclosed.

Comparatively few isolated starch grains will be seen in this case if the sample consists of pepper only, but foreign starches will be easily visible. Rice starch alone presents any difficulty owing to its small size and general resemblance to pepper starch. The granules of the latter vary from 0.5 to 5 $\mu$  in diameter, are polygonal or round and show a distinct hilum under a high power. Those of rice, of similar shape, vary from 2 to 10 $\mu$  in diameter and are also collected in aggregates which are never entirely broken up, and when the sample is examined in polarised light are easily picked out in the dark field from amongst the pepper masses by their much more brilliant appearance.

In examining microscopically for olive stones and for excess of pepper husk it is of advantage to obtain the coarser and heavier particles and examine them under a low power. This may be done by sifting the sample through a 60 mesh sieve, by sedimentation, or by removal of the starch by boiling with dilute hydrochloric acid. The structure of the particles may be rendered more easily visible by digesting for 2 or 3 days in chloral hydrate or by treatment with dilute nitric acid and potassium chlorate.

The most conspicuous structural elements of the outer shell are the spiral vessels and the hypodermal stone cells of the pericarp, distinguished from the stone cells of the endocarp (beaker cells) by their larger and more variable size (15 to 20 $\mu$  and sometimes 100 $\mu$  long), less regular shape, thicker walls and yellow brown colour. The polygonal beaker cells have pitted walls and are colourless.

In examining white pepper for added shell, care must be taken to see that the above-mentioned structures of the outer layer are present in substantial quantities. The inner layer is a normal part of the white pepper, and may be found in considerable quantities in the cheaper grades, where its presence is regarded by the trade as legitimate, although the addition of the dietetically much more valuable outer pericarp is looked upon as an adulteration.

With polarised light, ground-olive stones are easily recognised as they stand out brightly in the dark field, and exhibit a reddish tint. Most of the structural elements of pepper remain almost dark, but long pepper exhibits a bluish tinge under these conditions.

Various methods of staining have been suggested which will render the presence of 'poivrette' visible to the naked eye, but they are used to greater advantage in conjunction with the microscope. Dilute caustic soda colours olive stones, and also bleached pepper husks bright yellow while pepper remains unchanged. A solution of aniline in strong acetic acid leaves pepper unaltered, but turns ground olive stones or almond shells yellow brown.

Mixed with a few drops of freshly made 1 p.c. solution of phloroglucinol in alcohol and a drop of concentrated hydrochloric acid added olive stones, almond shells and substances containing much lignified tissue are stained pale to dark red, while pepper is only slightly altered to the naked eye. (For other reactions, see Analyst, xx. 1895, 181.)

**Chemical analysis.** For the routine chemical examination, the ash and the ash insoluble in HCl should be first estimated, the analyst being guided as to further determinations by the results of the microscopic examination.

If the total ash is estimated in the case of black pepper or 3 in the case of white pepper, added mineral matter may be suspected, and a more detailed analysis is required. The composition of the ash of pepper is as follows:—

TABLE II.

## ASH OF PEPPER.

(Rottger, Arch. f. Hygiene, 1886, Bd. IV. 183, and Blythe.)

No. of samples	Black pepper.		White pepper.	
	4.		2.	
	Per cent.		Average.	
K <sub>2</sub> O . . . . .	24.4 to	34.7	6.13	
Na <sub>2</sub> O . . . . .	1.5 "	5.5	0.79	
CaO . . . . .	11.6 "	16.1	33.09	
MgO . . . . .	3.3 "	13.0	10.59	
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.3 "	2.2	2.04	
MnO <sub>2</sub> . . . . .	0.19 "	0.8	0.55	
P <sub>2</sub> O <sub>5</sub> . . . . .	8.5 "	11.1	30.05	
SO <sub>3</sub> . . . . .	4.0 "	9.6	3.50	
Cl . . . . .	5.4 "	8.5	0.72	
Silica or sand . . . . .	1.5 "	6.5	2.05	
CO <sub>2</sub> . . . . .	14.0 "	20.0	10.96	

The amount of foreign starch can only be arrived at indirectly by calculation from the proportion of fibre, or pentosans, or fixed ether extract. On account of the somewhat wide variations in the composition of genuine pepper, no single determination affords trustworthy evidence.

If ground olive stones, almond shell, or similar substances have been detected, the most useful determinations are those of the fibre and starch. The starch should be determined by the diastase method after previous extraction with alcohol and ether, or by Ewer's method (J. Inst. Brewing, 1898, 552). The fibre by boiling 2 grms. of the sample under an inverted condenser with 200 c.c. of 1.25 p.c. sulphuric acid, and, after filtering and washing, extracting for a like period with the same volume of 1.25 p.c. soda, the fibre being finally filtered, dried, and weighed on a tared filter or Gooch crucible. The ash should be deducted. (For a quick method, which, however, gives different results from the above, see Stokes, Analyst, 12, 14.) If the fibre in a white pepper much exceeds 5 p.c. and microscopical examination shows the presence of the outer portions of the shell, the excess of husk may be taken as roughly equal to the percentage of fibre less 5 multiplied by 3.

For special purposes, the estimation of the

piperine may be required and should be carried out as follows:—

The dried alcoholic extract from 50 grms. of the sample is treated with caustic alkali to dissolve resins, etc., well washed on a filter with the same solution, then with water; the precipitate is next dissolved in alcohol, the latter evaporated and the residue redissolved in a small volume of alcohol, the piperine precipitated by the addition of water and collected on a tared filter, washed, dried, and weighed.

In the case of non-nitrogenous adulterants, the proportion of nitrogen affords a useful basis for calculation, as the nitrogen, other than that present in the piperine, is fairly constant in amount in genuine peppers. It is best, therefore, to determine total nitrogen by the Arnold-Gunning method (*i.e.* mixing 1 grm. of the sample with about the same weight of copper sulphate and red oxide of mercury and digesting with sulphuric acid and potassium sulphate in the usual manner for the ordinary Kjeldahl process). The nitrogen in the ether extract should then be determined in the same manner and deducted from the total nitrogen. The nitrogen figure for the ether extract, multiplied by 20.36, gives a rough measure of the piperine.

The following tables show the results of the analysis of pepper and of some of the most likely organic adulterants.

TABLE III.

Results of analyses of various varieties of Black and White pepper and of pepper shells by Winton, Ogden, and Mitchell; Winton and Bailey (An. Rep. Connect. Exp. Station 1898, 198-199; 1903, 158-164); and by Doolittle, Mich. Dairy and Food Dept., Bull. 34.

No. of samples . . . . .	Black pepper 65			White pepper 35			Pepper shells 7	
	Max.	Min.	Average	Max.	Min.	Average	Max.	Min.
Moisture . . . . .	12.95	8.09	10.26	14.47	8.04	10.90	11.01	7.00
Ash, total . . . . .	8.04 <sup>1</sup>	3.09	5.02	4.28	0.86	1.71	28.81	7.82
Ash, insoluble in HCl . . . . .	2.59 <sup>1</sup>	0.0	0.61	0.86	0.0	0.17	22.90	0.79
Ash, soluble in water . . . . .	3.32	1.65	2.52	1.16	0.12	0.38	4.66	1.53
Starch (Diastase method) . . . . .	41.75	22.05	35.64	63.60	48.88	54.97	15.30	2.30
Ether extract, volatile . . . . .	2.20	0.65	1.29	0.95	0.49	1.04	1.11	0.68
" " non-volatile . . . . .	10.44	6.60	7.90	7.94	5.65	6.58	4.97	1.51
Fibre . . . . .	18.89	10.05	11.88	7.65	0.10	3.87	32.15	21.06
Nitrogen, total . . . . .	2.53	1.86	2.15	2.14	1.85	1.99	2.33	1.72
Nitrogen in fixed ether extract . . . . .	0.45	0.25	0.32	0.34	0.24	0.30	0.15	0.20
	in 20 samples			in 10 samples			in 3 samples	
Alcohol extract . . . . .	11.86	8.31	9.44	8.55	7.19	7.66	6.30	4.00

TABLE IV.

Analysis of pepper adulterants. (Campbell Brown, Analyst, 1887, 12, 24.)

—	Ash	Starch	Fibre	Soluble in boiling dilute acid	Soluble in dilute alkali
White poivrete . . . . .	1.33	none	48.48	38.32	14.08
Black " " . . . . .	2.47	none	47.09	34.55	17.66
Ground " almond . . . . .	2.05	none	51.68	23.53	24.79
Ground olive stones . . . . .	1.61	none	45.38	39.08	15.04

Standards. The United States standards for pepper are as follows:—

	Black pepper.	White pepper.
	Not to exceed	
Ash . . . . .	7.0 p.c.	4.0 p.c.
Ash insol. in hydro-chloric acid . . . . .	2.0 "	0.5 "
Fibre . . . . .	15.0 "	5.0 "
	not less than	
Starch . . . . .	25.0 "	50.0 "
Fixed ether extract . . . . .	6.0 "	6.0 "
Percentage of N. in fixed ether extract . . . . .	4.0 "	3.25 "

Achein pepper, which often contains hollow kernels and shell in excess, were only the same kind. As a standard the maximum figures would be—Ash 7.00 p.c.

Black pepper should be free from added pepper shells, pepper dust, and other pepper.

Long Pepper is the fruit of *Piper officinarum* (Miq.) C.DC. and *P. longum* (Linn.) (N. O. *Piperaceae*) which grows in the islands of the Malay archipelago, Bengal, and the Philippine islands.

The fruit spike has the form of catkins from 2 to 6 cm. long and 4 to 7 mm. wide in the case of *P. officinarum*, that of *P. longum* being shorter and broader. It consists of numerous minute berries disposed along and partly embedded in an elongated axis. It has an odour and flavour somewhat resembling ordinary pepper but weaker and less agreeable, the smell becoming decidedly objectionable on warming.

It contains about the same amount of volatile oil and about half the amount of piperine present in ordinary pepper, and owing to the fact that the fruit often trails on the ground the ash is liable to be high, owing to the inclusion of clay and sand from the adherent soil, to remove which no special steps are taken. The figures obtained by the analyses of five samples by Campbell Brown and by Winton, Ogden, and Mitchell, are as follows:—

	Max.	Min.
Total ash . . . . .	9.61 p.c.	8.10 p.c.
Ash insol. HCl. . . . .	0.22 "	0.15 "
Ether extract . . . . .	7.24 "	4.90 "
Starch and matters convertible into sugar . . . . .	49.34 "	42.88 "
Fibre . . . . .	15.70 "	5.76 "
Nitrogen . . . . .	2.30 "	2.00 "
Alcohol extract . . . . .	8.67	
Starch by diastase . . . . .	39.55	

It does not come into the retail market, and its chief use is in the pickling and canning trade, and, formerly, at all events, for the adulteration of black and white pepper (*q.v.*), for which purpose it may be bleached.

It has been used medicinally as a stimulant and carminative. C. H. C.

**PEPPER, CAYENNE.** Cayenne pepper is the dried and powdered fruit of various small fruited species of *Capsicum* of which *C. fastigiatum* (Blume) and *C. frutescens* (Linn.) are the most important. The plant is indigenous in tropical America and is cultivated in hot and temperate climates in many parts of the world.

The fruit is elongated, conical, and has a shiny, bright red surface becoming dull red and shrivelled when dry. The pods are from  $\frac{1}{2}$  to 2 cm. long and contain numerous yellowish, flattened kidney shaped seeds, 3 to 4 mm. in diameter.

Paprika, a large fruited variety of *Capsicum annuum*, is grown in Hungary, Spain, Italy, France, and Turkey. The fruit is from 2 to 5 cm. long and has a bright red or yellow shiny surface, but has not the intensely hot and pungent flavour of cayenne pepper. It is used chiefly on the Continent.

Other varieties of *C. annuum* are also widely employed on the Continent and in America for pickling.

Pimiento is a large fruited pepper of bright red colour and very mild flavour, used for stuffing olives and as colouring matter.

**Composition.** The characteristic constituents

are a red colouring matter, present only in the pod, soluble in ether, light petroleum, carbon disulphide, or chloroform, and an active principle *capsaicine*,  $C_{15}H_{25}NO_3$ , to which the characteristic flavour is mainly due, and which, though it preponderates in the pod, is also found in the seed (Micko, Zeitsch. Nahr. genussm. 1, 818; 2, 411). There is also a tasteless and odourless fixed oil and an oleoresin (*syn. capsinin*), which, as used in medicine, is a mixture of fat, resin, and various other substances extracted by the solvent employed (Alcohol, B.P. Codex; Acetone, U.S. Pharmacopeia). Analyses by Richardson (U.S. Depart. of Agric., Div. of Chem. Bull. 13, 1887) of *Capsicum annuum* yielded the following results:

TABLE I.

	Seed	Pod	Fruit
Loss at 100° C. . . . .	8.12	14.75	11.94
Albuminoids (N $\times$ 6.25) . . . . .	18.31	10.69	13.88
Fat (ether extract) . . . . .	28.54	5.48	15.26
Fibre . . . . .	17.50	23.73	21.09
Ash . . . . .	3.2	6.62	5.20

Cayenne pepper is mainly used as a condiment and also in canary and chicken foods. The whole fruit, ripe or unripe, appears in the market as capsicums or chillies, low grade fruits of large size being usually employed under these names for pickling, etc. The dried fruit of *Capsicum minimum* is 'official' in the British Pharmacopeia. It acts as a stomaehic and alimentary canal, externally as an irritant and vesicant.

**Adulteration.** Although a long list of adulterants is given in most text-books, cayenne pepper is rarely sophisticated in this country at the present time. The addition of foreign starches, such as wheat and rice, of mineral substances, gypsum and red ochre and, to mask the presence of light-coloured adulterants like starch and gypsum, such diverse materials as turmeric, ground redwood, and aniline dyes should still be looked for. Ground nutshells and olive stones have also been found comparatively recently.

**Detection of adulteration.** Microscopical examination will suffice to detect the adulterants of vegetable origin. The presence of foreign starches will be at once apparent. The very minute starch grains of cayenne pepper are only present in very small numbers, the quantity being dependent on the ripeness of the fruit when gathered, and are usually embedded in cells.

The microscopical appearance of cayenne pepper is very characteristic and comparison with a standard sample will enable any of the above-mentioned vegetable adulterants to be detected with comparative ease (*v. PEPPER*).

Preparations of the sample, both before and after removal of the fat, should be mounted in water or dilute glycerol. Fragments of the epicarp showing quadrilateral cells of which the walls have a slightly wavy outline, but are not beaded, and which are arranged in rows, serve to distinguish cayenne pepper from paprika. (For further details as to the structural differences between different species of capsicums, see Pharm. J. 1901, 13, 552; 1902, 69, 3; or Winton, Microscopy of Vegetable Foods.)

The presence of mineral adulterants will be indicated by a high ash; nutshells or olive stones will raise the proportion of fibre (estimated as in Pepper, *q.v.*). For the detection of oil, soluble vegetable or coal tar colours, the ether extract of the sample may be shaken with a mixture of 2 parts of carbon disulphide and 15 parts of ethyl alcohol. The carbon disulphide will dissolve the oil and the natural colouring matter of the capsicum, while most aniline colours will pass into the supernatant alcohol layer.

Table II. (Parry, "Food and Drugs") shows the limits within which the figures obtained by the analyses of cayenne pepper are found to vary, and Table III. gives figures for chillies and Table IV. for paprika.

TABLE II.

	Maximum	Minimum
Moisture . . . . .	7.5	3.5
Ether extract, volatile . . . . .	2.8	0.7
" " non-volatile . . . . .	15.5	19.0
Alcohol extract . . . . .	30.0	25.0
Starch by diastase method . . . . .	1.5	0.8
Fibre . . . . .	25.0	20.0
Nitrogen . . . . .	2.40	2.08
Ash, total . . . . .	7.2	5.0
" soluble in water . . . . .	3.3	0.30
" insoluble in HCl . . . . .	0.3	0.05

TABLE III.

Analyses of whole chillies. (Zanzibar, Japan and Bombay. 8 samples in all.) (Winton, Ogden and Mitchell, Ann. Report, Connecticut Exper. Station, 1898, 200.)

	Maximum	Minimum	Average
Moisture . . . . .	7.08	3.67	5.73
Ether extract, volatile . . . . .	2.57	0.73	1.35
" " non-volatile . . . . .	21.81	17.17	20.15
Alcohol extract . . . . .	27.61	21.52	24.35
Starch (diastase method) . . . . .	1.46	0.80	1.01
Fibre . . . . .	24.91	20.35	22.35
Nitrogen, total . . . . .	2.34	2.13	2.18
Ash, total . . . . .	5.96	5.08	5.45
" soluble in water . . . . .	4.93	3.30	3.98
" insol. in HCl . . . . .	0.23	0.05	0.15

TABLE IV.

Analyses of whole pods. (Doolittle and Ogden, J. Soc. 30, 1908, 1481.)

	Maximum	Minimum	Average
Loss at 100°C. . . . .	9.39	7.28	8.52
Ether extract, volatile . . . . .	1.25	0.17	0.93
" " non-volatile . . . . .	11.99	7.42	9.57
Iodine number . . . . .	136.8	130.3	133.5
Reducing matters (acid conversion) as starch . . . . .	21.4	16.52	19.46
Fibre . . . . .	19.83	15.1	15.33
N×6.25 . . . . .	17.44	14.06	15.51
Ash total . . . . .	7.06	5.24	6.22
" soluble in water . . . . .	5.79	4.59	5.14
" insol. HCl . . . . .	0.22	0.05	0.08
Alkalinity of ash, total . . . . .	8.00	6.10	7.04
" " sol. in water . . . . .	5.70	4.07	4.93

**Standards.** The official standard of the U.S. Department of Agriculture for cayenne pepper provides that it shall be the dried ripe

fruit of *C. frutescens*, *C. baccatum*, or any small fruited species of capsicum, and that the fixed ether extract should not be below 15 p.c., the total ash not more than 6.5 p.c., the ash insoluble in HCl not more than 0.5 p.c., starch (diastase method) not more than 1.5 p.c., and fibre not more than 28 p.c.

C. H. C.

**PEPPERMINT.** The *Mentha piperita* (Linn.) of Europe and America; *M. arvensis* (Linn.) of Japan. Extensively grown for the sake of its volatile oil, which is procured by distilling its leaves. The oil and the preparations made from it are used as aromatics, carminatives, and stimulants, and are useful in medicine for griping pains. It is also employed in the form of mint-camphor, or menthol, for outward application in affections of the nerves (*v.* OILS, ESSENTIAL).

Oil of peppermint amounts on the average to 0.8 of the total plant used. The crystals of peppermint oil are obtained from the distillate after the oil having been drained off, the process is repeated, when a tolerably pure oil is secured. After a third repetition no crystallisation takes place.

**Menthol**, or peppermint-camphor, in its commercial state is a white crystallised mass, melting at about 35° and boiling at 210°. When purified by distillation the melting-point is raised to 42° and the boiling-point to 212°.

**Menthone**  $C_{15}H_{26}O$  is a colourless mobile liquid, neutral to test papers, soluble in almost all proportions in alcohol, chloroform, benzene, and carbon disulphide, but insoluble in water. It stands to menthol in a similar relation to that in which camphor stands to borneol, as is shown by the fact that menthol can be reproduced from its ketone  $C_{15}H_{26}O$  by a reaction similar to that by which borneol is produced from camphor.

**Menthene**  $C_{10}H_{18}$  is a colourless liquid of an agreeable odour, moderately soluble in ether or alcohol, more so in benzene, turpentine, and petroleum. It may be prepared by heating menthol with zinc chloride. See J. Moss (Pharm. J. [iii.] 5, 554; J. Med. Soc. Lond. [iii.] 5, 825); Beckett and . . . . . Trans. 1876, 1, 1); M. Moriya . . . . .; Atkinson and Yoshida (*ibid.* 1882, 41, 49) (*v.* *Peppermint camphor*, art. CAMPHORS *v.* TERPENES).

**PEPPERMINT CAMPHOR** *v.* CAMPHORS.

**PEPPERMINT OIL** *v.* OILS, ESSENTIAL.

**PEPSIN.** *Pepsinum* (Pepsine, Fr.; *Pepsin*, Ger.). Pepsin is a ferment or enzyme, existing in the acid secretion of the mucous membrane of the stomach or gastric juice. It possesses the property, in presence of dilute acid, and, within certain limits of temperature, of converting albuminous food into soluble assimilable peptone. Schwann (Müller's Arch. 1836) made the first attempt to prepare the ferment in a form available for supplying artificial digestion in cases where the natural function was imperfectly performed. To obtain a good product and to preserve it requires great care and skill. The animals generally selected are the hog, sheep, and calf, and the preparation usually employed is simply the dried mucous membrane of the stomach. Details of preparation are given by Beale (Med. T. Gaz. 1872, 1, 152), Wasmann (Lehm. Phys. Chem. 2, 40), Brücke (Sitz. Ber. 43, 601), Schmidt (Annalen, 61, 22), Liebreich (Practitioner, March 1877), Petit (J. Pharm. Chim. [v.] 2, 85),

Chapoteaut (Compt. rend. 95, 140), Maly (J. pr. Chem. [ii.] 11, 104), Wittick (J. 1870, 894), Meissner (Z. Rat. Med. 7, 1; 8, 280; 10, 1; 12, 46; 14, 78 and 303); also Scheffer (Amer. J. Pharm. 42, 98; 43, 3; Pharm. J. [iii.] 1, 666; 2, 761, 783), Seldon (*ibid.* [iii.] 4, 89), Long (Med. Press. Cir. 8, 300), Kinkad (Lancet, 1870, 2, 667), Farr (Med. T. Gaz. 1871, 1, 302), Rennard (J. 1874, 944), Zwick (Amer. J. Pharm. 43, 261), Audouard (Year-Book Pharm. 1878, 343), Pekelharing (Zeitsch. physiol. Chem. 22, 233), Nencki and Sieber (*ibid.* 32, 291), Schrumphf (Beit. chem. Physiol. Path. 6, 396).

Pepsin of commerce varies much in activity (Tuson, Lancet, 1870, 2, 212; Grierson, Year-Book Pharm. 1887, 263). 5 milligrams digested with 12.5 grams of coagulated and firm white of fresh eggs and 125 c.c. of acidified water containing about 0.2 p.c. of hydrogen chloride at 40-5° for 6 hours with frequent shaking should give an almost clear solution, containing only a few small flakes. This method of testing, which is adopted by the Pharmacopœia, is the outcome of numerous investigations as to the effect of different temperatures and different forms of albumen, together with the selection of an acid and determination of its appropriate strength. Compare Petit (J. Pharm. Chim. [v.] 1, 82; 2, 85), Bengier (Pharm. J. [iii.] 12, 270, 415), Grützner (Zeitsch. anal. Chem. 1874, 106), Vigier (J. Pharm. Chim. [v.] 19, 398; 9, 461; 10, 17), Schlickum (Year-Book Pharm. 1886, 96), Dastre (Compt. rend. Soc. Biol. 1894, 778), Croner (Virchow's Archiv. 150, 289), Harlay (J. Pharm. Chim. [vi.] 10, 105).

Peptic activity is inhibited or destroyed by antiseptics (Grober, Pflüger's Archiv. 104, 109), certain bacteria (Papasotiriou, Arch. Hygiene, 57, 269), or by shaking (Shaklee and Meltzer, Proc. Amer. Physiol. Soc. 1908, 29).

In addition to the method given above, various other methods have been devised for the determination of peptic activity (Samojloff, Pflüger's Archiv. 85, 86; Meunier, J. Pharm. Chim. [vi.] 14, 555; Kuttner, Zeitsch. physiol. Chem. 52, 63; Fuld and Levison, Biochem. Zeitsch. 6, 473; Einhorn, Chem. Zentr. 1908, ii. 1295).

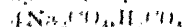
On the question of the identity of pepsin and rennin, see Schmidt-Nielsen (Zeitsch. physiol. Chem. 48, 92), Gewin (*ibid.* 54, 32), Bang (*ibid.* 54, 359), Hammarsten (*ibid.* 56, 18), Herzog (*ibid.* 60, 298), Taylor (J. Biol. Chem. 5, 399).

A. S.

**PERCARBONATES**  $M_2C_2O_6$ , may be prepared by electrolysis a strong solution of the normal carbonates at -30° to -40° (Riesenfeld and Reinhold, Ber. 1909, 42, 4377). The potassium salt is a bluish-white, amorphous deliquescent powder which decomposes on heating into potassium carbonate, carbon dioxide and oxygen, and is a strong oxidising and bleaching agent. When added to a neutral solution of potassium iodide, it liberates iodine thus:  $K_2C_2O_6 + 2KI + 2H^+ \rightarrow 2K_2CO_3 + I_2$ ; no oxygen being evolved. The above authors regard this action as characteristic for the percarbonates, and therefore maintain that the 'percarbonates,' such as  $Na_2CO_3$ , obtained by the action of hydrogen peroxide on sodium carbonate (Tanatar, Ber. 1899, 32, 1544; J. Russ. Phys. Chem. Soc. 1902, 34, 952), are additive compounds of carbonates and hydrogen peroxide. This con-

tention is, however, denied by Tanatar (ib. 1910, 43, 127, 2149; see also Wollenstein, ib. 639; Riesenfeld, *ibid.* 566, 2591).

The only percarbonates which have been prepared are those of the alkali metals, and barium (Wollenstein and Felner, Ber. 1908, 4, 271). Sodium hydrogen percarbonate



has been used as a disinfectant and in the preparation of hydrogen peroxide (D. R. P. 18559).

**PEREZONE.** An alcoholic solution of pipitzonic acid obtained from the rhizome of *Piper adnata* (A. Gray), found in Mexico. It is extremely sensitive to alkalis, which destroy it rose-mary and may be used as an indicator.

**PERFUMES (SYNTHETIC).** Prior to 18<sup>th</sup> perfumes were prepared almost entirely in plants by various processes of distillation or extraction (c. OULÉ, *Essence*), much and even used from the very earliest time, were of animal origin; synthetic perfume was unknown. Today, almost every flower perfume may be imitated by a so-called 'synthetic oil,' the odor of which closely resembles that of the natural product. The faithfulness of the imitation varies very much with the different odors; is doubtful, for instance, whether any pure synthetic violet or rose oil is present in nature can vie with the natural fragrance. The term 'synthetic' thus applied is misleading; if 'synthetic oils' are in fact mixtures of a number of chemical compounds, some of which have been obtained by synthetic processes, others merely isolated from the essential oils in which they occur. In many cases, the most satisfactory results are only obtained by blending the 'synthetic' with a natural oil. The jasmine oil is added with good effect to the 'synthetic' oils of rose, lilac, nymphaea, &c. the ketone (jasmine) characteristic of ylang oil has been isolated, but its composition has as yet been determined, and no synthetic substance hitherto obtained is entirely satisfactory in replacing it. In certain cases where the constitution of the characteristic constituent of a particular perfume has not been elucidated the substitute may consist of a substance possessing an entirely different structure from that of the natural product yet closely resembling it in smell. Thus the characteristic principle of musk is a non nitrogenous ketone of unknown constitution; synthetic musk consists, however, of various derivatives of tertiary butyl alcohol.

The synthetic perfume industry may be said to have originated with the manufacture of vanillin from coumarin, described in a paper taken out by Tiemann in 1870 (Eur. Pat. 1161 shortly afterwards in 1879, coumarin and heliotropin were prepared, and since that time the production of synthetic substances for use in the blending of perfumes has steadily continued.

Not only in the case of an oil modified by the presence of minute traces of essential substances, but the degree of dilution is an important factor in producing the proper odour. The solvent most commonly used is 95-96 p.c. ethyl alcohol. The carbocation the alcohol is of great importance; it must be free from fixed oil; and taste, smell, ap-



colour must give no indication of impurities. Methyl alcohol finds little application, largely owing to the fact that the commercial alcohol contains more or less acetone, which has an injurious effect. 95 p.c. alcohol is also used for preparing the infusions of the flower pomades, 1250 kilos. of solvent being used to extract 1000 kilos. of pomade. The extraction is twice repeated so that three infusions are obtained, diminishing in strength. For the cheaper sorts of extracts and toilet-waters, the rectified spirits of wine is replaced by potato spirit.

The least soluble of the synthetic perfumes are the artificial musks, of which less than 1 p.c. dissolves in alcohol. Benzyl benzoate and benzyl cinnamate are used as solvents for these, 1 kg. of the former dissolving 500 grams ketone moschus or 250 grams Musc Baur.

The extracts which are sold as handkerchief perfumes are known as quadruple, triple, double, and simple, according to their strength; 12 parts of a triple extract will furnish 20 parts of double or 30 parts of simple extract by dilution with alcohol and water; in the preparation of the double and simple extracts, the second infusions of the flower pomades are also utilised.

For the preparation of aqueous and dilute alcoholic toilet waters, only a limited number of substances are available, owing to the sparing solubility of the majority of perfumes in water. The most soluble are phenyl ethyl alcohol (2 p.c.), benzyl alcohol (1 p.c.) and vanillin (0.8 p.c.).

*Relation between constitution and smell.*—Our knowledge of the relations between the constitution of a compound and its odour is very scanty. Within the same class of compounds, there is a general resemblance, and there is a gradual change of odour in passing from one member of a homologous series to the next, well-marked, for instance, in such a series as that of the fatty esters. Austerweit and Cochin (Compt. rend. 1910, 150, 693) have studied the effect of the alkyl substituents on the geraniol and citronellol molecules. In citronellol, the introduction of one methyl or ethyl group is accompanied by a marked odour of tea roses: a second methyl or ethyl group is described as giving an odour of roses with a faint ... But if the substituent ... radicle, the rose odour ... phenyl be the entering radicle, the rose odour is much augmented. In geraniol, the introduction of one or two methyl groups produces a smell of pelargonium leaves; the ethyl group appears to leave unaltered the odour of the original geraniol. The effect of the position of the aldehyde group in the ... ring was studied ... work on ionone ... 366, 119). Their conclusion is that aldehydes which are derived from cyclogeraniolene form with acetone products possessing the odour of violets if the aldehyde group is adjacent to the methyl groups. The intensity of the odour increases with the number of methyl groups which are adjacent to the aldehyde group; if, however, the latter be removed from the proximity of the methyl groups, the odour vanishes. In his work on the nitrobutylxylones (Artificial Musks), Baur has also studied the effect of the

position of the substituents in the benzene nucleus on the smell (Ber. 24, 2832). It is, however, difficult to draw any general conclusions: we are met with startling anomalies, such as the well-known resemblance between the odours of benzaldehyde and nitro-benzene, and little can be said save that the part played by unsaturated groupings is important. The subject is particularly difficult to investigate, since our sensation offers only a vague means of classifying and measuring smell.

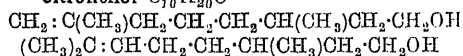
The list of substances, used in the compounding of perfumes is a long one. The most important of these are as follows:

**Hydrocarbons.** With the exception of styrene and *p*-cymene, the hydrocarbons which occur in the natural perfumes and contribute to their odour belong to the terpene group. Pinene, with its characteristic odour of pine-needles, is the chief constituent of pine-needle oil; *d*-limonene occurs in the oils of lemon, orange, orange-flower, bergamot, &c.: menthene is found in oil of peppermint and carvene in caraway oil (*v. TERPENES*). The halogen derivatives and  $\alpha$ -chloro- and  $\alpha$ -bromo-styrene are used in the preparation of oil of hyacinth.

**Alcohols.** The saturated fatty alcohols occur commonly as esters; the alcohols of the terpene and of the aromatic series are either free or in combination with fatty acids. The latter are used in preparing ... others, the oils of rose, jasmine, ...

#### OLEFINIC TERPENE ALCOHOLS.

##### Citronellol $C_{10}H_{20}O$



b.p. [*d*-citronellol] (17 mm.)  $117^\circ-118^\circ$ ; sp.gr. 0.8565 at  $17.5^\circ$ ;  $[a]_D + 4^\circ$  at  $17.5^\circ$ ;  $n_D 1.45679$ ; b.p. [*l*-citronellol] (15 mm.)  $113^\circ-114^\circ$ ; sp.gr. 0.8612 at  $20^\circ$ ;  $[a]_D - 4^\circ 20'$ ;  $n_D 1.45789$  (Tiemann and Schmidt, Ber. 1896, 29, 906).

*d*-Citronellol occurs in geranium and in Java citronella oils; ... been isolated from geranium and from rose-oils. Prolonged discussion has taken place as to the identity of citronellol with the alcohols, 'rhodinol,' 'reunil,' and 'roseol' isolated from geranium or rose-oil. It is now accepted that the last two are mixtures of citronellol with geraniol. The evidence as to the chemical identity of the *l*-rhodinol, described by Barbier and Bouveault (Compt. rend. 1897, 124, 1308), is somewhat conflicting, for Schimmel & Co. (Report, Oct. 1904, 123) showed that citronellol obtained by the reduction of citronellal gave a pyroacetic ester, the semi-carbazone of which was identical with that similarly obtained from rhodinol, each melting at  $110^\circ-111^\circ$ . The most satisfactory explanation of the discrepant results obtained by different observers appears to be that recently offered by Harries and Himmelmann (Ber. 1908, 41, 2187), who, from studying the action of ozone on the citronella compounds, arrived at the conclusion that citronellol consists of a mixture of two isomerides, differing in the position of the double bond as represented above. By the action of ozone on citronellol, 20 p.c. of acetone

is produced corresponding to 20 p.c. of the rhodinol structure  $(CH_3)_2C=C<$ . The evidence for the formula of citronellol is based chiefly upon the behaviour of the corresponding aldehyde, citronellal (*v. infra*).

Citronellol occurs in company with geraniol: the boiling-points of both alcohols lie very close to each other, but geraniol is the less stable and may be destroyed by heating with phthalic anhydride at 200° or with benzoyl chloride at 140°-160° (Barbier and Bouveault, Compt. rend. 1896, 121, 530). Citronellol may be obtained from citronella oil by reducing with sodium amalgam and acetic acid when the aldehydes citral and citronellal are reduced to citronellol. The mixture of geraniol and citronellol is then treated with phosphorus trichloride in ethereal solution at a low temperature: a phosphite of citronellol is formed which is extracted by water, geranyl chloride remaining in the ethereal layer (Tiemann, Ber. 1896, 29, 921).

Cold dilute  $KMnO_4$  oxidises citronellol to a polyhydric alcohol, converted by chromic acid mixture to acetone and  $\beta$ -methyl adipic acid. It is characterised by a liquid phthalic acid ester giving a crystalline silver salt, and by its oxidation to citronellal, the latter being identified by its semi-carbazone (m.p. 84°) or its compound with  $\beta$ -naphthocinchoninic acid.

The isomeric alcohols of the formula  $C_{10}H_{18}O$ , *linalool*, *geraniol*, and *nerol*, readily undergo mutual transformation. Thus if geraniol be heated at 200° with water in an autoclave, linalool is formed (Schimmel Report, April, 1898, 25). When treated with hydrochloric acid, geraniol is converted into linalyl chloride, from which linalool may be obtained by the action of alcoholic potash or of a solution of silver nitrate (Tiemann, Ber. 1898, 31, 832; 1895, 28, 2138). On the other hand, by the action of acetic anhydride on linalool, a mixture of the acetates of *geraniol*, *nerol*, and *terpineol* is formed (Tiemann, Ber. 1895, 28, 2137; Tiemann and Semmler, *ibid.* 1893, 26, 2714; Stephan, J. pr. Chem. 1898, [iii.], 58, 109; Zeitschel, Ber. 1903, 39, 1780). They frequently occur together and have all three been detected in the oils of rose, neroli, petit grain and linaloe.

**Linalool**  $C_{10}H_{18}O$   
 $(CH_3)_2C:CH:CH_2:CH_2:C(CH_3)(OH)CH:CH_2$  or  
 $CH_3:C(CH_3)CH_2:CH_2:CH_2:C(CH_3)(OH)CH:CH_2$   
 b.p. 198°-199° (13 mm.) 88.3°-89.5°: sp.gr. 0.870  
 at 15°,  $n_D^{20}$  1.4668 (Gildmeister, Arch. Pharm. 1895, 233, 179); *l*-linalool  $[\alpha]_D -20^\circ 7'$ : *d*-linalool  $[\alpha]_D +19^\circ 8'$  (Stephan).

Linalool is the chief constituent of linaloe oil; it occurs as the *l* form in the oil from Cayenne, and both as *d* and *l* forms in that from Mexico. Amongst other oils in which it has been detected are coriander (*l*), sweet orange (*d*), nutmeg (*d*), ylang-ylang (*l*), rose (*l*), reunion geranium (*l*), petit-grain (*l*), bergamot (*l*), neroli (*l*), lemon (*l*); in the four last of these and in lavender and jasmine-flower oils, it is also present as the acetate; the butyrate occurs in lavender oil and the isobutyrate in Ceylon cinnamon oil and the isovalerate in the oil of sassafras leaves. It is isolated by fractional distillation and

purified by the action of phthalic anhydride on its sodium compound; *l*-linalool is soluble in water and with alcoholic potash, the linalool may be extracted with ether. Citral is obtained by oxidation with chromic acid mixture (Bertram and Waldbaum, J. pr. Chem. 1892, [ii.] 45, 599).

Dilute  $KMnO_4$  in the cold oxidises it to polyhydric alcohols, which are converted by chromic acid mixture into acetone and laevulic acid (Tiemann and Semmler, Ber. 1895, 28, 2130); by reduction with nickel and hydrogen, 2:6-dimethyl octane has been obtained (Ber. 1908, 41, 2083).

It may be identified by its phenyl urethane (m.p. 65°-66°) or its  $\alpha$ -naphthyl urethane (m.p. 53°) or it may be oxidised to citral.

#### Geraniol $C_{10}H_{18}O$

$(CH_3)_2C:CH:CH_2:CH_2:C(CH_3):CH:CH_2:OH$   
 b.p. (17 mm.) 120.5°-122.5°; sp.gr. 0.8894 at 20°;  $n_D^{20}$  1.4766 (Tiemann and Semmler, Ber. 1893, 26, 2711).

Geraniol forms the chief constituent of Palmarosa and of German and Turkish rose oils and occurs in geranium, citronella, lemongrass, and many other oils. It is also found as acetate, isovalerate, *n*-caproate, and tiglate. It is isolated by fractional distillation and purified either by means of its crystalline compound with calcium chloride (Bertram and Gildmeister, J. pr. Chem. 1896, [ii.] 53, 233; 1897, 56, 507), or by treating its sodium compound with phthalic anhydride in benzene solution (Tiemann and Krüger, Ber. 1896, 29, 1901). By oxidation with chromic acid mixture, citral is obtained (Tiemann, Ber. 1898, 31, 828), from which geraniol may again be obtained by reduction. The catalytic action of copper at a high temperature has also been utilised for the oxidation of geraniol to citral (Bouveault, Bull. Soc. chim. 1903, [iv.] 3, 119). The action of chromic acid mixture after treating with  $KMnO_4$ , produces acetone, laevulic, and oxalic acids (Semmler, Ber. 1893, 26, 2720). Geraniol is more stable than linalool to the action of acids and is quantitatively converted by acetic anhydride into geranyl acetate. By the action of dilute  $H_2SO_4$ , terpin hydrate is obtained (Tiemann and Schmidt, *ibid.* 1895, 28, 2138): concentrated formic acid reacts forming  $\alpha$ -terpineol, terpinene and dipentene (Bertram and Gildmeister, J. pr. Chem. 1894, [ii.] 49, 195; Stephan, *ibid.* 1899, [ii.] 60, 244). The phthalic acid ester (m.p. 47°), the  $\alpha$ -naphthyl urethane (m.p. 47°-48°), and the di-phenyl urethane (m.p. 124°) are characteristic.

**Nerol**  $C_{10}H_{18}O$ , stereoisomeric with geraniol; b.p. 226°-227°: 125° (25 mm.); sp.gr. 0.8813 at 15°; occurs in neroli-oil, chiefly as acetate (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 502), in rose, linaloe, and petit grain oils, and in the oil of *Helichrysum angustifolium* (Heine & Co., D. R. P. 209382). It may be obtained by the action of acetic anhydride on linalool (Zeitschel, Ber. 1906, 39, 1780): about 5 p.c. is formed on reducing citral. It has a rose-like smell and in chemical behaviour resembles geraniol. Nerol does not, however, give a crystalline compound with  $CaCl_2$  and reacts with dilute  $H_2SO_4$ , forming terpin hydrate more readily than does

geraniol. Its di-phenyl urethane melts at 52°-53°.

#### CYCLO TERPENE ALCOHOLS.

**Terpineol** *v.* TERPENES.

**Borneol** *v.* CAMPHORS.

**isoBorneol** *v.* CAMPHORS.

#### AROMATIC ALCOHOLS.

**Benzyl alcohol**  $C_6H_5 \cdot CH_2OH$ ; b.p. 205°, sp.gr. 1.05 at 15°,  $n_D^{20}$  1.540; occurs free in tuberose, ylang ylang, carnation, jasmine oils, &c., as acetate in ylang ylang, hyacinth, and jasmine oils, as benzoate (ylang ylang), cinnamate, salicylate (ylang ylang), and phenyl acetate (neroli). It is manufactured by the action of lead oxide at 100° or of potassium carbonate on benzyl chloride, or by the action of potassium acetate and saponification of the acetate formed. It is characterised by a phenyl urethane (m.p. 78°), a phthalic acid ester (m.p. 106°-107°), and a semi-carbazone of its pyroracemic ester (m.p. 176°).

**Phenyl ethyl alcohol**  $C_6H_5 \cdot CH_2 \cdot CH_2OH$ ; b.p. 220°-222° (740 mm.), sp.gr. 1.2042 at 15°,  $n_D^{20}$  1.53212; occurs in rose and neroli oils as benzoate and salicylate. In preparing rose-oil by the action of benzyl chloride on the phenyl ethyl alcohol is lost. It is obtained by reducing (1) phenyl acetaldehyde with sodium amalgam, and (2) phenyl acetic ester with sodium and alcohol; in its manufacture other methods are probably used. It is purified by means of its compound with calcium salicylate (Bouveault and Blanc, D. R. P. 164294; Compt. rend. 1903, 136, 1676; 1903, 137, 60). It may be separated from citronellol and geraniol by its greater solubility in dilute alcohol. The phenyl urethane melts at 80°, the phthalic acid ester at 188°-189°.

**Phenyl propyl alcohol**  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ ; b.p. 235°, sp.gr. 1.007 at 15°. This alcohol, hyacinth-like in odour, is obtained by reducing cinnamic ester with sodium and alcohol (Schimmel, D. R. P. 116091) or by reducing benzyl aceto-acetic ester (Bouveault and Blanc, D. R. P. 164294). The phenyl urethane melts at 47°-48°.

**Cinnamic alcohol** (*v.* CINNAMIC ALCOHOL).

#### ESTERS.

The methods used in the preparation of the esters are (1) the action of hydrochloric acid on a mixture of alcohol and acid; (2) the action of the alcohol or its sodium compound on the fatty acid anhydride or chloride, the reaction on the large scale being carried out in pyridine solution.

In preparing the esters of those olefinic terpene alcohols which themselves undergo change on heating with acid reagents, a mixture of the alcohol and acid may be treated with small quantities of a mineral acid below 30° (Bertram, D. R. P. 80711).

The fatty acid esters find wide application as fruit essences. A list of those more especially used in perfumery is appended.

Ester	Boiling-point	Synthetic oil in which used
Bornyl formate	90° (10 mm.)	Lime blossom
Citronellyl "	97°-100° (10 mm.)	Geranium
Geranyl "	119°-121° (15 mm.)	"
Amyl acetate	112° (760) 38° (12 mm.)	"
Benzyl "	262° (760)	Jasmine
Bornyl "	98° (10 mm.)	"
Geranyl "	128°-129° (16 mm.)	Rose
Linalyl "	97° (10 mm.)	Bergamot
Phenyl ethyl "	"	Orange flower
Terpineol "	110°-115° (10 mm.)	Bergamot, Lilac
Geranyl propionate	"	Bergamot
Geranyl butyrate	"	"
Geranyl caproate	"	Geranium
Ethyl cinnanthylate	"	"
Ethyl pelargonate	"	"

A large number of patents deal with the preparation of the esters of the cyclic terpene alcohols: thus in preparing *isoborneol* esters, camphene and the fatty acid may be heated with  $P_2O_5$  (Schindelmeyer, D. R. P. 229190), pinene hydrochloride warmed with the fatty acid, and anhydrous zinc sulphate (D. R. P. 196017), &c.

Amongst the aromatic acid esters used are:

Ester	Boiling-point	Synthetic oil in which used
Methyl benzoate	199.2° (746 mm.)	Ylang - ylang, hyacinth
Ethyl "	211°	Ylang-ylang
Benzyl "	"	largely used as a solvent for non-alcoholic perfumes, e.g. artificial musks
Phenylethyl, Linalyl	"	Hyacinth
Methyl salicylate	217° (730 mm.)	Ylang-ylang
Ethyl "	234° (743 mm.)	Oil of winter-green
Amyl "	276°-277° (743 mm.)	Clover

The esters of the unsaturated and ketonic fatty acids also find considerable application. The  $\alpha\beta$ -unsaturated acids, e.g. nonylenic acid, may be prepared by condensing aldehydes with malonic acid in pyridine solution (Weizmann and Harding, Chem. Zentr., 1910, 97, 299).

The acetylene carboxylic acids are prepared by acting on the sodium acetylene hydrocarbons with  $CO_2$  in ethereal solution. Heptine ( $C_7H_{12}$ ) and octine ( $C_8H_{14}$ ) are thus converted to *octinic* and *noninic* acids; on boiling these with alcoholic caustic potash, esters of  $\beta$ -ketonic acids are obtained (Moureu, D. R. PP. 132802, 1902; 133631; 158252, 1905).

These esters are also directly prepared by treating the sodium compounds of the hydrocarbons with chloroformic ester in ethereal solution.

#### PHENOLS AND THEIR ETHERS.

**isoEugenol** (*v.* EUGENOL).

**Anethole** (*v.* ANETHOLE).

**Thymol** (*v.* PHENOL AND ITS HOMOLOGUES).

**Naphthol** (*v.* NAPHTHALENE).

The methyl and ethyl  $\beta$ -naphthyl ethers are both known as *nerolin*, the former as *yara-yara*,

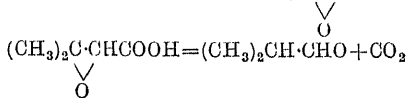
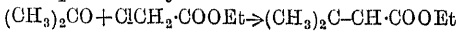
the latter as bromelia. In very dilute solution, the odour resembles that of orange-flower.

#### ALDEHYDES.

General methods used for the production of higher fatty aldehydes are—

(1) The reduction of the ester of the corresponding acid to the alcohol and subsequent oxidation of the alcohol, heated copper being used as the catalytic agent.

(2) The method of Darzens (D. R. P. 174239, 174279), by which a ketone is condensed with chloroacetic ester in the presence of an alkaline condensing agent; on heating the glycidic acid thus obtained, CO<sub>2</sub> is evolved and the aldehyde formed. A large number of aldehydes have been produced by this method.



Higher fatty aldehydes have been detected in oils of rose, lemon, &c.

*n*-Octaldehyde C<sub>8</sub>H<sub>16</sub>O; b.p. 60°–63° (10 mm.), sp.gr. 0.827 at 15°, *n*<sub>D</sub> 1.41955. Prepared from octyl alcohol (Schimmel, Rep. 1899, 25). The β-naphthyl cinchoninic acid derivative melts at 234°.

*n*-Nonaldehyde C<sub>9</sub>H<sub>18</sub>O; b.p. 80°–82° (13 mm.), sp.gr. 0.8277 at 15°, *n*<sub>D</sub> 1.42452. First detected in rose-oil (Schimmel, Rep. 1900, 53) and subsequently in orris, cinnamon, mandarin and lemon oils.

A yield of 71 p.c. is obtained by distilling α-hydroxydecanoic acid (Bugard, Bull. Soc. chim. 1907, iv. 346; Bouveault and Blanc, Compt. rend. 136, 1903, 167). Identified by the oxime (m.p. 69°), semi-carbazone (m.p. 100°); yields pelargonic acid (b.p. 252°) on oxidation.

*n*-Decaldehyde C<sub>10</sub>H<sub>20</sub>O, b.p. 93°–94° (12 mm.), 207°–209° (755 mm.), sp.gr. 0.828 at 15°, *n*<sub>D</sub> 1.42977 (Stephan, J. pr. Chem. 1900, [ii.] 62, 525). Occurs in orris, neroli, mandarin and other oils. A yield of 52 p.c. is obtained by distilling α-hydroxyundecylic acid. The oxime melts at 69°, semi-carbazone at 102°, β-naphtho-cinchoninic acid compound at 237°.

#### OLEFINIC TERPENE ALDEHYDES.

**Citral** (geranial), C<sub>10</sub>H<sub>16</sub>O

(a) (CH<sub>3</sub>)<sub>2</sub>C:CH-CH<sub>2</sub>-CH<sub>2</sub>-C(CH<sub>3</sub>):CH-CHO  
(b) CH<sub>3</sub>:C(CH<sub>3</sub>)CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C(CH<sub>3</sub>):CH-CHO  
b.p. 110°–112° (12 mm.); sp.gr. 0.8972 at 15°, *n*<sub>D</sub> 1.4931. Occurs in lemon grass, citronellol, rose, and many other oils, as two stereoisomeric forms (a) and (b) (chiefly as the former), giving semicarbazones melting respectively at 164° and 171° (Tiemann, Ber. 1899, 32, 115). On oxidising geraniol with chromic acid mixture, a 30–40 p.c. yield of citral is obtained, and it is also formed when linalool and nerol are oxidised. It has been synthesised by distilling a mixture of the calcium salts of geranic and formic acids. On heating with acids, it is converted into geranone (Tiemann, Ber. 1899, 32, 115). It is also converted into geranone by soda, methyl heptenone and acetaldehyde are formed. Oxidation with chromic acid mixture converts it into methyl heptenone, but if first

oxidised with cold permanganate and then with chromic acid, acetone and laevulic acid result. In acetic acid solution, it is reduced by sodium amalgam to geraniol. The action of sodium bisulphite produces different compounds according to the conditions (Tiemann, *ibid.* 1898, 31, 3317). The normal compound from which the citral may again be regenerated by the action of alkalis, is formed in the presence of a small quantity of sulphurous acid. The β-naphtho-cinchoninic acid compound (m.p. 200°) is used for its

**Citronellal** C<sub>10</sub>H<sub>18</sub>O

(CH<sub>3</sub>)<sub>2</sub>C:CH-CH<sub>2</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)CH<sub>2</sub>:CHO  
CH<sub>2</sub>:C(CH<sub>3</sub>)CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)CH<sub>2</sub>:CHO  
b.p. 205°–208°, 103°–105° (25 mm.); sp.gr. 0.8538 at 17.5°, *n*<sub>D</sub> 1.4481, *n*<sub>D</sub> 12° 30'. Occurs chiefly in citronella oil. It is reduced by sodium amalgam to citronellol; the action of acids results in closing the ring, isopulegol being formed. The action of sodium bisulphite has been studied by Tiemann (Ber. 1898, 31, 3305). By adjusting the conditions, methods of separating citral and citronellal have been devised. Thus whilst citral reacts with dilute solutions of sodium bisulphite and bicarbonate, citronellal reacts only with concentrated solutions (Ber. 1899, 32, 815). Much discussion has taken place as to the identity of natural citronellal with the compound obtained by oxidising rose-oil. The latter compound being designated by Barbier and Bouveault as rhodinal. The conversion of rhodinal to menthone under the influence of acids is affirmed by Barbier and Bouveault (Compt. rend. 1896, 122, 737; 1904, 138, 1699; Bull. Soc. chim. 1900, [iii.] 23, 458), although denied by Tiemann and Schmidt (Ber. 1897, 30, 38).

Harries and Himmelmann (Ber. 1908, 41, 2187) have since shown that in citronellal the two isomeric compounds formulated above are present. The semicarbazone (m.p. 82.5°) and β-naphthyl cinchoninic acid compound (m.p. 225°) are characteristic.

#### AROMATIC ALDEHYDES.

**Benzaldehyde** C<sub>6</sub>H<sub>5</sub>:CHO (v. BENZALDEHYDE).

**Phenyl acetaldehyde** C<sub>6</sub>H<sub>5</sub>:CH<sub>2</sub>:CHO; b.p. 75° (5 mm.), sp.gr. 1.0315 at 15°, *n*<sub>D</sub> 1.52536 (Schimmel and Co.). This may be obtained from phenyl chlor (or α-brom) lactic acid or from phenyl and α-brom-styrol. In the latter case agents it is converted into the phenyl acetaldehyde. It is unstable and tends to polymerise on keeping.

**Cinnamaldehyde** C<sub>6</sub>H<sub>5</sub>:CH:CH:CHO (v. CINNAMIC ALDEHYDE).

**Salicylaldehyde** C<sub>6</sub>H<sub>4</sub>(OH):CHO (v. SALICYLIC ALDEHYDE).

**Anisaldehyde** C<sub>6</sub>H<sub>4</sub>(OCH<sub>3</sub>):CHO, *p*-methoxy benzaldehyde (Aubépine); b.p. 248° (corr.), 91° (4 mm.), sp.gr. 1.126–1.129 at 15°, *n*<sub>D</sub> 1.672.

Prepared by the oxidation of anise oil, consisting



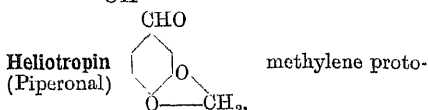
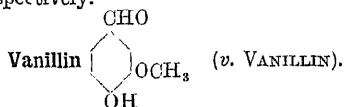
chiefly of anethole



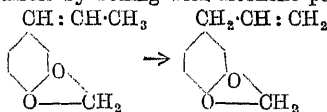
with about

10 p.c. of the isomeric estragole. The oxidising

agents used are dilute nitric acid, chromic acid mixture or ozone. It is also obtained by the methylation of *p*-hydroxyacetophenone. The semi-carbazone m.p. 132°. The two modifications of the oxime at 63° and 132° respectively.



catechuic aldehyde. White crystals, m.p. 36°; b.p. 236°. Heliotropin has the characteristic odour of heliotrope flowers, but it has only been detected in the flowers of *Spiraea ulmaria* (Linn.). It was originally synthesised by Fittig and Mielk from piperonylic acid, and was prepared from piperine. Ground pepper is mixed with slaked lime and water, evaporated to dryness and extracted with ether. The residue is boiled with alcoholic potash and the potassium piperate formed oxidised with permanganate. From the filtered solution, heliotropin crystallises out. It is now manufactured by the oxidation of isosafrol with chromic acid. The product is extracted with ether and purified by means of its bisulphite compound. The yield produced by oxidation of safrole is much less, so that the safrole is converted first to isosafrole by boiling with alcoholic potash.



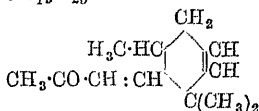
The use of ozone as oxidising agent gives a good yield of a pure product (Otto). It may also be prepared by the action of methylene iodide on protocatechuic aldehyde in presence of alkali.

Since its introduction in 1879, the price has fallen from £150 to 30s. per kilo. It must be kept in a cool, dark place since it becomes gradually discoloured on exposure to light; in the hot weather it is not stable in alcoholic solution. It may be prepared by a semicarbazone (m.p. 224°-225°), by reduction to piperonyl alcohol (m.p. 51°), or by oxidation to piperonylic acid (m.p. 228°).

#### KETONES.

The most important members of this class are irone, the odoriferous principle of orris-root ionone, the basis of the synthetic violet perfumes, and jasmone, the ketone isolated by Hesse from jasmine oil, the constitution of which is as yet unknown.

Irone  $C_{13}H_{20}O$

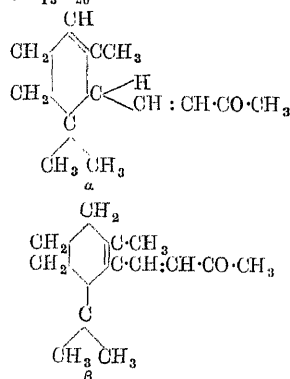


b.p. 144° (16 mm.); sp.gr. 0.939 at 20°,  $[\alpha]_D^{20} +40^\circ$ ,  $n_D^{20}$  1.50113 (Tiemann and Kruger).

The orris root is extracted with ether and the extracted matter distilled in steam. The volatile fraction contains irone, myristic, and oleic acids and their esters and oleic aldehyde. The acids and esters are removed by treating with alcoholic potash, the aldehydes oxidised by means of silver oxide, and finally the irone separated by conversion into its phenyl hydrazone (Tiemann and Kruger, Ber. 1893, 26, 2675). It may be obtained more conveniently from orris-root oil by fractional distillation. The smell of the pure substance is sharp when concentrated, but if largely diluted, resembles that of violets. Its synthesis has been accomplished by Merling and Welde (Annalen, 1909, 366, 119) who, starting from isopropylidene acetacetic ester, succeeded in obtaining  $\Delta^4$ -cyclocitral; on condensing this with acetone, irone was produced.

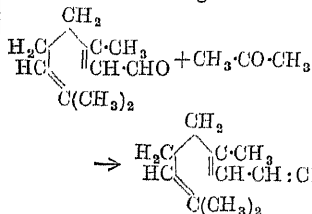
It is characterised by a *p*-bromophenyl hydrazone (m.p. 174°-175°), and an oxime (m.p. 121.5°), crystallising with difficulty.

Ionone  $C_{13}H_{20}O$



$\alpha$ -Ionone, b.p. 123°-124° (11 mm.), sp.gr. 0.932 at 20°,  $n_D^{20}$  1.4980;  $\beta$ -Ionone, b.p. 127°-128.5° (10 mm.), sp.gr. 0.946 at 17°,  $n_D^{17}$  1.521.

Ionone, obtained by Tiemann and Krüger (Ber. 1893, 26, 2691) in an unsuccessful endeavour to synthesize citral, forms the basis of synthetic ionone. Citral and acetone interact, in the presence of alkaline condensing agents, forming *pseudo*-ionone, a pale yellow strongly refractive oil, boiling at 143°-145° (12 mm.).



This, when treated with acids, is converted into a mixture of the isomeric cyclic ketones  $\alpha$ - and  $\beta$ -ionone. As the alkaline condensing agent dilute baryta water may be used, or the dry mixture of citral and acetone may be shaken with dry sodium peroxide (Kayse, D. R. P. 127661), or with  $PbO$ ,  $LaO$ , or borates (Haarman and Reimer, D. R. P. 130457). The proportion of  $\alpha$ - or  $\beta$ - compound produced

depends on the nature of the acid chosen to effect the closing of the ring. Concentrated sulphuric acid, or the prolonged action of dilute acids produces chiefly the  $\beta$ -compound, concentrated phosphoric or formic acids almost entirely the  $\alpha$ -derivative.  $\alpha$ -Ionone is transformed by the  $\beta$ -compound.

devised for the separation of the  $\alpha$ - and  $\beta$ -forms. If the mixed bisulphite compounds be distilled in steam,  $\beta$ -ionone distils over; the  $\alpha$ -compound remains behind in combination and is liberated on the addition of alkali. The difference in solubility of the semicarbazones may also be utilised.

$\alpha$ -Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 142°–143°).

$\beta$ -Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 116°–118°).

The semicarbazones melt respectively at 107°–108° ( $\alpha$ ) and 148° ( $\beta$ ).

A large number of patents deal with the preparation of similar products. Homologues of acetone and other ketones may replace acetone (Fr. Pat. 269884). Ivalderine is thus produced by condensing with methyl ethyl ketone, ianthone with methyl penterone (Fr. Pat. 278333), ganthone with mesityloxide (D. R. P. 118288). Calcium chloride and iron chloride have also been used as condensing agents. The characteristic violet odour of these compounds only becomes apparent in dilute solutions.

Ionone hydrate and its homologues prepared by condensing citral hydrate with acetone are also described (Coulin, D. R. P. 198483, 200654).

#### LACTONE.

**Coumarin** (*v.* COUMARIN) has the scent characteristic of new mown hay.

#### OXIDE.

**Cineol** (*v.* CAMPHORS).

#### COMPOUNDS CONTAINING NITROGEN.

**Indole**, a constituent of jasmine flower oil (*v.* INDOLES).

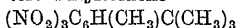
**Scatole** occurs in civet (*v.* INDOLES).

**Methyl anthranilate**, m.p. 24°–25°; b.p. 132° (14 mm.), sp.gr. 1.168 at 15°. Occurs in neroli, tuberose, ylang-ylang, jasmine flower, bergamot and other oils. It consists of white crystals which show a blue fluorescence; solutions are also fluorescent.

**Methyl methylanthranilate**, m.p. 18.5°–19.5°; b.p. 130° (13 mm.), sp.gr. 1.120 at 15°. Occurs in mandarin oil.

**Nitrobenzene** is used as a substitute for bitter almond oil.

**Trinitro-tert.-butyltoluene**

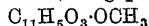


(Tonquinol or Musc Baur), pale yellow crystals (m.p. 96°–97°). Prepared by condensing *iso*-butyl chloride with toluene in the presence of  $\text{AlCl}_3$  and nitrating the product formed; during the process, the *isobutyl* is transformed to tertiary butyl. The butyl toluene is added to 5 times its weight of a mixture of 1 part  $\text{HNO}_3$  (1.5) and 2 parts fuming  $\text{H}_2\text{SO}_4$  containing 15 p.c. anhydride and heated at 100° for 8–9 hours.

#### THE USE OF SYNTHETIC SUBSTANCES IN THE BLENDING OF PERFUMES.

By suitably mixing and diluting the compounds enumerated above, a great variety of perfumes may be produced and many of the natural oils and extracts imitated. The exact composition of these substitutes varies with the particular maker and is kept as a trade secret. As far as possible, a knowledge of the composition of the natural oil serves as a guide in choosing the constituents; in the blending of perfumes the best results appear to be obtained by the addition of both natural and synthetic products. Thus, in the group of perfumes, jasmine, lilac, muguet, &c., jasmine oil is added to a mixture of synthetic substances.

**Bergamot.** The natural oil contains about 38 p.c. of linalyl acetate: other constituents are limonene, di-pentene, linalool, camphene, octylene, acetic acid (Burgess and Page, Chem. Soc. Trans. 1904, 85, 1327), and two substances of unknown constitution, bergaptene



(Pomeranz) and bergaptine, a coumarin-like substance, melting at 59.5° (Soden and Rojahn, Pharm. Zeit. 46, 778). The main constituent of the synthetic oil is linalyl acetate; terpineol acetate, geranyl propionate, and geranyl methyl ether are also used in its preparation.

**Carnation.** Eugenol, *isoeugenol*, caryophyllene are used as ingredients of oil of carnation.

**Hawthorn.** The scent of the hawthorn is faithfully reproduced by anisaldehyde (Aubépine).

**Heliotrope.** Attempts to identify heliotropin in the extract of heliotrope flowers have failed; the odour of synthetic heliotropin closely resembles that of the heliotrope flower and is the basis of all the heliotropes. Its odour is improved by the addition of coumarin and vanillin and by blending with rose or jasmine oil.

**Hyacinth.** Enklaar (Chem. Weekblad, 1, 1910, 7) identified benzyl alcohol, benzyl benzoate, and ethyl cinnamate in the essential oil of hyacinth; he failed to detect methyl anthranilate. Cinnamic alcohol is especially characterised by a hyacinth-like smell. The following constituents are used in preparing an oil of hyacinth: phenyl ethyl alcohol, cinnamic alcohol, phenyl ethyl aldehyde, methyl benzoate, phenyl ethyl acetate, methyl and ethyl cinnamates, terpineol, and  $\alpha$ -chlor- and  $\alpha$ -brom-styrolenes.

**Jasmine.** The oil extracted from the pomade obtained from jasmine flowers by the process of enfleurage was shown by Hesse to have the following composition (Ber. 1899, 32, 2611).

Benzyl acetate	. . .	65.0 p.c.
Linalyl acetate	. . .	7.5 "
Benzyl alcohol	. . .	6.0 "
Linalool	. . .	16.0 "
Indole	. . .	2.5 "
Methyl anthranilate	. . .	0.5 "
Jasmone (a ketone $\text{C}_{11}\text{H}_{16}\text{O}$ )	. . .	3.0 "

The methyl anthranilate cannot be extracted directly from the plant, but appears to be formed during the process of enfleurage. By distillation with steam, 0.4 p.c. methyl anthranilate

was obtained. The oil obtained by distilling the fresh flowers was found to be free from indole (Hesse, Ber. 1904, 37, 1457).

Elze (Chem. Zeit. 1910, 34, 912) found, in addition to the above, cinnamyl acetate, geraniol, *p*-cresol, and *p*-cresyl methyl ether. The synthetic oil consists chiefly of benzyl acetate and benzyl alcohol to which cinnamic acetate, linalool and its acetate, indole and methyl anthranilate may be added. The substance peculiarly characteristic of the jasmine scent appears to be the ketone jasmone, which cannot yet be obtained synthetically. A proportion of jasmine oil is added to the mixture of synthetic substances, as the oil prepared only from synthetic substances is not entirely satisfactory.

**Lilac.** Terpineol is the characteristic constituent of lilac perfumes. Commercial terpineol is prepared by the action of dilute acids on terpin hydrate, the fraction boiling up to 216°, being known as terpinol and terpinolene, above 216° as terpineol. Commercial terpineol is obtainable both in the solid and liquid forms, the latter having the more intense odour. It contains *l*-linalool and terpinolene.

**Lily of the Valley (Muguet).** Terpineol is also used as a constituent of the lily of the valley perfumes with geraniol and citronellol. A mixture of 90 p.c. terpineol and 10 p.c. palma rosa oil has a strong muguet odour. Linalool, benzyl alcohol and its acetate are amongst the other constituents employed.

**Musk.** Natural musk, obtained from an abdominal gland of the musk deer (*Moschus moschiferus*), owes its characteristic odour to a ketone, muscone ( $C_{15}H_{30}O$  or  $C_{15}H_{28}O$ ); the distillate obtained on distilling the secretion in steam is extracted with ether, treated with alcoholic potash, washed with water and finally distilled *in vacuo*. The ketone passes over in the fraction boiling at 145°–147° (3 mm.). Muscone is now sold in alcoholic solution. As early as 1759, Margraff had obtained a product smelling of musk by treating amber with nitric acid. In 1878, von Gerichten observed the musk-like odour of chlor- and brom-nitrocymenes and three years later, Kolbe prepared another musk-scented compound, di-nitro-*m*-cymene. In 1888, Baur took out the first patents for the preparation of artificial musk and has since made an exhaustive study of the groups in the benzene ring conditioning the musk-like odour. Two nitro-groups must be present, and a third negative group symmetrically arranged; the three other positions are filled by alkyl groups, of which one must be a tertiary radicle. A large number of these artificial musks, di-nitro- or tri-nitro-derivatives of tert-butyl-toluene or -xylene, have been introduced. The most important of these are

Musc Baur	} Trinitro-tert-butyltoluene
Moschus	
Tonquinol	
Musk ketone	Trinitro tertiary-butylxylene
	Dinitro-tert-butyl- <i>m</i> -xylylmethyl ketone
Musk aldehyde	Dinitro-butyl- <i>m</i> -xylyl aldehyde

**Orange-flower** (synthetic neroli oil). The

composition of a specimen of the natural oil is given as follows (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 481):—

	p.c.
Hydrocarbons (pinene, camphene, dipentene and a paraffin $C_{27}$ )	35.0
Terpene alcohols and acetates—	
<i>l</i> -Linalool	30.0
<i>l</i> -Linalyl acetate	7.0
<i>d</i> -Terpineol	2.0
Geraniol and nerol	4.0
Geranyl and neryl acetates	4.0
<i>d</i> -Nerolidol	6.0
Methyl anthranilate	0.6
Acetic and palmitic acids	0.1
Indole	0.1
Resin and loss (decylic, phenyl acetic acids, &c.)	11.2
	100.0

Methyl and ethyl  $\beta$ -naphthyl ethers are employed as substitutes for neroli oil; a mixture of the two was originally introduced as nerolin, the former is now known as yara-yara, the latter as bromelia. In the composition of the synthetic oil, geraniol, linalool, nerol, and their acetates with methyl anthranilate are used. A solution of 40 grams of the synthetic oil in 1 kg. of alcohol constitutes the tincture used as the equivalent of the first infusion of the flower pomade.

**Rose.** The natural oil was shown by Markownikoff in 1891 (Ber. 23, 3191) to consist of an inodorous hydrocarbon, stearoptene, melting at 36.5° and a liquid portion, eleoptene, from which two substances, having the composition  $C_{19}H_{18}O$  and  $C_{10}H_{20}O$ , could be separated. In the same year, Poleck and Eckart (*ibid.* 23, 3554) showed that the liquid constituent  $C_{19}H_{18}O$  (rhodinol) was identical with geraniol, isolated by Semmler from Indian geranium oil and constituting 66–74 p.c. of German and 80–88 p.c. of Turkish rose oil. The presence of citronellol ( $C_{10}H_{20}O$ ) was established by Tiemann (Ber. 29, 921), who, by treating the alcohols at a low temperature with  $PCl_5$  in ethereal solution, obtained a phosphite of citronellol, geranyl chloride remaining in the ethereal solution. These two alcohols form the main constituents of rose oil and of such preparations as roseol, reunol, &c. In 1900, it was shown that the extract of fresh rose-leaves contained about 2 p.c. of phenyl ethyl alcohol. This was present to a much less extent in the oils obtained by steam distillation, owing probably to the loss of the sparingly soluble alcohol in the steam distillate. In addition to the above alcohols, small amounts of linalool, citral, and nonaldehyde were detected (Walbaum, Ber. 1900, 33, 2299, 2302; *cp.* Soden and Rojahn, *ibid.* 1900, 33, 3063; Schimmel, Rep. 1900, 53). The substances enumerated above are used in the manufacture of synthetic rose oil. Up to the present, the scent of the oil prepared entirely from synthetic substances cannot rival the fragrance of the natural product. The most successful preparations contain some proportion of the natural oil or of the tincture made from the natural extract, to which some synthetic rose oil and such substances as neroli oil, vanillin, musk, or

her synthetic compounds may be added at the discretion of the perfumer. Extensive adulteration of the natural oil takes place at the source of production, e.g. in Bulgaria, the geraniol and citronellol from cheaper oils, such as geranium, ulma rosa, being added and distilled with the rose oil.

**Violet.** The basis of the artificial violet perfumes is ionone or some closely allied substance. The scent of  $\alpha$ -ionone is stated to be sweeter and more penetrating, resembling more closely that of orris root; that of the  $\beta$ -compound resembles more closely the natural violet. After smelling a natural violet extract or a dilution of ionone for some little time, the odour often cannot be perceived, the nasal nerve endings being easily fatigued by this scent. The smell of violets is only apparent when the pure substance is diluted. Ionone was originally placed on the market as a 10 p.c. alcoholic solution, 10 grams of which gave 1 kilogram of violet tincture. Now the pure substances, consisting of 100 p.c.  $\alpha$ -ionone and 100 p.c.  $\beta$ -ionone respectively are obtainable. Irones and derivatives of ionone also find application. With the violet tincture so prepared, other tinctures made both from natural and synthetic oils are blended: rose, jasmine, orris, ylang-ylang, are amongst those thus used. As instances of violet scents prepared from natural and synthetic substances, the following may be quoted (Mann, Moderne Parfumerie):—

grms.	Spring violet.	grms.	Violet scent.	
1000	Infusion violets, I.	5000	Tincture ionone	Synthetic
1000	" rose, I.	1000	" rose-oil	
750	" jasmine, I	1000	" jasmine	
250	" acacia	300	" orange	
50	Tincture coumarin	3000	" iris oil	
50	Infusion benzoin	50	" musk	
50	" musk	10	Ylang-ylang oil	
100	Solution rose oil	200	Infusion benzoin	
100	Tincture vanillin			
40	" ylidoron			

**Ylang-ylang oil.** The oil extracted from the flowers of *Cananga odorata* (Hook.) (v. OILS, ESSENTIAL) contains about 30–32 p.c. linalool, 9 p.c. linalyl benzoate, 7 p.c. linalyl acetate, a little geraniol, and about 30 p.c. of a hydrocarbon, sabinene. Methyl alcohol and *p*-cresyl acetate have also been detected (Darzens, Bull. Soc. chim. 1902, 27, 83). Bacon identified in addition formic acid and isosafrol (Schimmel, Rep., Oct. 1908). In the composition of the artificial oil, the following compounds occur; linalool, geraniol, methyl and ethyl benzoates, linalyl and geranyl benzoates, benzyl salicylates and other esters. Bacon (l.c.) also examined a number of esters with reference to their suitability as constituents of this oil.

**New mown hay.** Coumarin forms the main constituent of this perfume and with it tinctures of orange, rose, jasmine, &c., are blended.

As instances of two well-known fancy perfumes, the following may be quoted (Mann, Moderne Parfumerie). These are, of course, subject to wide variation.

grms.	Peau d'Espagne.	grms.	Ess bouquet.
50	Cassie flower oil	2000	Tincture of rose, I.
100	Sandalwood oil	1000	" cassie, I.
60	Niobe oil	1000	" tuberose, I.
200	Bergamot oil	2550	Extract of reseda
1000	Tincture of musk	2000	" bergamot
1500	" civet	10	Rosewood oil
1000	Infusion of tolu	50	Bergamot oil

Peau d'Espagne.

grms.  
40 Vetiver oil  
10 Turan oil  
10,000 Spirit

Ess bouquet.

grms.  
100 Infusion of musk, I.  
50 Tincture of civet  
100 Infusion of tolu  
3 Turan oil

**Eau de Cologne.** This, one of the oldest and most famous of perfumes, was manufactured in Cologne at the end of the seventeenth century. It is disputed whether Johann Maria Farina or Paul de Feminis of Milan, both of whom came from Italy to Cologne, was the original inventor; in both cases the secret was bequeathed to their successors, that of Paul de Feminis passing to his nephew, Johann Anton Farina: there are now three firms bearing the name Farina who claim to possess the original formula and who zealously guard it. The general nature of the preparation of Eau de Cologne is, however, known, although details of the preparation may be lacking. The quality of the spirit used is of paramount importance: only the most highly purified spirits of wine may be used, and after the perfume is prepared, it must be left for a long time, some years if possible, to mature. The firms who possess the original secret continue to use the same ingredients and are not concerned with synthetic oils. Other perfumers make use of such synthetic oils as nerol and bergamot, with those of rosemary, lemon, lavender, and petit-grain; the composition of each Eau de Cologne varies considerably. A typical example is as follows:—

30,000 grams spirit.

100	" neroli oil.
30	" rosemary oil.
100	" Mitcham lavender oil.
300	" lemon oil.
300	" bergamot oil.
50	" petit grain oil.

(See OILS, ESSENTIAL; Gildemeister und Hoffmann, Die Aetherischen Oele, 1910, Otto, Les Parfums; Mann, Die Moderne Parfumerie; &c.) I. S.

**PERHYDROL.** Trade name for a solution of hydrogen peroxide (q.v.).

**PERICLINE v. FELSPAR.**

**PERILLA OIL.** Perilla oil occurs to an extent of 35–8 p.c. in the nuts of *Perilla ocymoides* (Linn.), an annual labiate, indigenous to the East Indies as also to China (Manchuria) and Japan. It is extensively grown in China and Japan, and is also cultivated in the Himalayas. The plant is sown in April, blossoms about the end of September, and ripens two weeks later. The seed is known in Japan as Ye-Goma, or Se-no-abura. For the physical and chemical characteristics, see tables under OILS, FIXED, AND FATS.

This oil has the highest iodine value of any known fatty oil, and simulates linseed oil in taste and smell. Endeavours have been made to import it into Europe as a substitute for linseed oil. J. L.

**PERMANGANATES v. MANGANESE.**

**PERNAMBUCO WOOD v. BRAZIL WOOD.**

**PEROVSKITE or PEROVSKITE v. TITANIUM.**

**PERONIN.** Trade name for the hydrochloride of morphine benzyl ester, used as a sedative (v. SYNTHETIC DRUGS).

**PEROXOLS.** Trade names for mixtures of hydrogen peroxide containing salicylic acid,



carbolic acid, menthol, &c.

#### PEROXYDASES *v.* FERMENTATION.

##### PERSEITOL *v.* CARBOHYDRATES.

**PERSIAN BERRIES** are the seed-bearing fruit of various species of *Rhamnus*, growing wild or cultivated in France, Spain, Italy, the Levant, and Persia. The Persian berry proper is obtained from *R. amygdalinus*, *R. oleoides*, and *R. saxatilis*, and is imported from Smyrna and Aleppo. Its size is about that of a pea, colour yellowish-green, surface much shrivelled, hard, and divisible along well-marked depressions forming a cross, into four parts, each containing a triangular seed; its taste is intensely bitter.

Avignon or French berries, the product of *R. infectorius* (Linn.) and *R. Alaternus* (Linn.), are smaller in size than the foregoing and contain only two seeds.

Spanish, Italian, and Hungarian berries are respectively the products of *R. saxatilis*, *R. infectorius* (Linn.), and *R. cathartica* (Linn.). These are similar in quality to the Avignon berries. Other qualities come from the Morea, Wallachia, and Bessarabia.

That all of these botanical varieties do not contain the same constituents appears certain from the work of Tschirch and Polacco (Arch. Pharm. 1900, 238, 459) and other chemists, on the *R. cathartica*; but, on the other hand, there is every reason to suppose that the colouring constituents of the botanical group to which the term Persian berry proper is applied are identical in each case.

Gelatly (Edinburgh New. Phil. Jour. 7, 252) was the first to isolate from Persian berries (*R. tinctoria* [Wald. et Kit.]) the glucoside *xanthorhamnin*  $C_{45}H_{56}O_{28}$ , which on hydrolysis with acid gave a sugar and a colouring matter *rhamnetin*. Hlasiwetz (Annalen, 112, 107) considered that xanthorhamnin was identical with *rhamnetin*, and *rhamnetin* with quercetin, but Böttger and Berteche (Bull. Soc. Ind. 1885, 3, 456) denied this, and assigned to *rhamnetin* the formula  $C_{12}H_{16}O_5$ . Xanthorhamnin, which Schützenberger (J. 1868, 774) termed *α-rhamnegin* was considered to possess the formula  $C_{24}H_{32}O_{14}$ . The presence of a second glucoside, *β-rhamnegin* was also detected by this chemist, and from this by hydrolysis *β-rhamnetin* was derived. Liebermann and Hörmann (Annalen, 196, 313) also investigated Persian berries, devised a method for the preparation of xanthorhamnin and *rhamnetin*, and prepared various derivatives of the latter.

It is now known that Persian berries contain the glucosides of three colouring matters, namely *rhamnetin*, *rhamnazin*, and *quercetin* (Herzig, Monatsh. 6, 889; 9, 549; 12, 175; Perkin and Geldard, Chem. Soc. Trans. 1895, 67, 500).

To isolate these substances Persian berries are extracted with boiling water, the solution treated with a small quantity of sulphuric acid, and digested while boiling for one hour. The glucosides are thus hydrolysed and the crude colouring matters separate in the form of a greenish-yellow precipitate.

The product is extracted with boiling alcohol, which dissolves principally the *quercetin*, this being the most soluble of the three colouring matters. The residue now contains *rhamnetin*

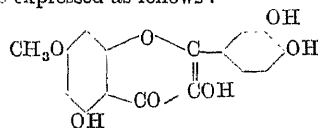
and *rhamnazin*, and the latter is removed from the former by two or three extractions with boiling acetic acid.

*Rhamnetin*  $C_{16}H_{12}O_7$  crystallises in yellow needles very sparingly soluble in acetic acid and alcohol. It dissolves in alkaline solutions with a pale yellow colour, and gives with alcoholic lead acetate an orange-red precipitate. When acetylated it forms *tetra-acetyl rhamnetin*  $C_{16}H_8O_7(C_2H_5O)_4$  (Liebermann and Hörmann), colourless needles, m.p. 183°–185°, and on bromination *dibromrhamnetin* is produced.

*Rhamnetin sulphate*  $C_{16}H_{12}O_7 \cdot H_2SO_4$  (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 650), orange-red needles, m.p. 183°–185°, and *potassium rhamnetin*  $C_{16}H_{11}O_7K$  (Perkin and Pate, ibid. 1895, 136), orange-yellow needles, have been prepared.

*Rhamnetin* is in reality a *quercetin monomethyl ether* (Herzig, l.c.), for on digestion with hydriodic acid it is converted into *quercetin*, and with methyl iodide *quercetin monomethyl ether* is produced.

*Rhamnetin* is soluble in potassium hydroxide solution, of which it forms a potassium salt, or by aspirating air through a solution, *rhamnetin* gives *protocatechuic acid*, and a syrupy phloroglucinol derivative. The latter, identified by means of its diazobenzene compound, consists of *phloroglucinol monomethyl ether* (Perkin and Allison, Chem. Soc. Trans. 1895, 81, 470), and consequently the constitution of *rhamnetin* is to be expressed as follows:



*Rhamnetin* is a strong dyestuff, and gives on mordanted woollen cloth shades which are practically identical with those produced by *quercetin*:

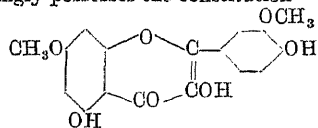
Chromium.	Aluminum.	Tin.	Iron.
Red	Brown	Bright	Deep
brown.	orange.	orange.	olive.

(Perkin and Wilkinson, *ibid.* 1902, 81, 590).

*Rhamnazin*  $C_{17}H_{14}O_7$  (P. and G.), yellow needles, m.p. 214°–215°, is moderately soluble in boiling toluene, a property which distinguishes it from both *rhamnetin* and *quercetin*. It is soluble in alkaline liquids to form orange-yellow solutions, and with alcoholic ferric chloride gives an olive-green colouration.

*Acetyl rhamnazin*  $C_{17}H_{11}O_7(C_2H_5O)_3$ , colourless needles, *benzoyl rhamnazin*  $C_{17}H_{11}O_7(C_6H_5O)_3$ , colourless needles, m.p. 204°–205°, and *dibromrhamnazin*  $C_{17}H_{12}Br_2O_7$ , yellow needles have been prepared.

*Rhamnazin* is a *quercetin dimethyl ether*. Digested with boiling hydriodic acid, it is converted into *quercetin*, and by means of methyl iodide into *quercetin tetramethyl ether*. Boiling alcoholic potash hydrolyses *rhamnazin* with formation of *vanillic acid* and *phloroglucinol monomethyl ether* (Perkin and Allison, l.c.). It accordingly possesses the constitution—



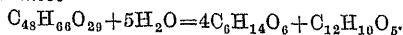
Rhamnazin does not readily dye mordanted calico, but on mordanted wool gives shades resembling those which are produced by kaempferol—

<i>Chromium.</i>	<i>Aluminium.</i>	<i>Tin.</i>	<i>Iron.</i>
Golden yellow.	Orange yellow.	Lemon yellow.	Olive brown.

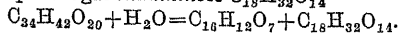
Only a small amount of this colouring matter is present in Persian berries.

**Xanthorhamnin**  $C_{34}H_{42}O_{20}$  is readily prepared by extracting powdered Persian berries with three times their weight of boiling 85 p.c. alcohol. On standing the dark brown filtered extract deposits a large quantity of the impure glucoside as a brown resinous mass. From the supernatant liquid on standing a purer xanthorhamnin separates in the form of pale yellow cauliflower-like precipitate, and in such quantity as to congeal the whole liquid to a stiff paste. This is collected, repeatedly crystallised from alcohol, and finally from alcohol containing a little water and ether (Liebermann and Hörmann, l.c.).

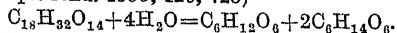
Xanthorhamnin consists of pale-yellow needles readily soluble in water and hot alcohol, soluble in alkaline solutions with a yellow colour. With basic lead acetate it gives an orange precipitate. According to the work of Liebermann and Hörmann, xanthorhamnin, when hydrolysed with acid, gives *rhamnetin* and *rhamnose*



More recently, however, xanthorhamnin has been shown to possess the formula  $C_{34}H_{42}O_{20}$ , and that by means of its specific ferment *rhamminase*, contained by Persian berries, it is hydrolysed with formation of rhamnetin and a complex sugar *rhamminose*  $C_{19}H_{32}O_{14}$



When rhamminose is digested with boiling dilute acids, it is converted into 2 molecules of *rhamnose*, and 1 molecule of *galactose* (C. and G. Tanret, Compt. rend. 1899, 129, 725)



No glucosides of rhamnazin or quercetin have been isolated as yet from Persian berries. The action of the ferment rhamminase is readily demonstrated. If crushed Persian berries contained in a muslin bag, are suspended in water heated to 40°, a yellow solution containing the glucosides is produced; this quickly becomes opaque and a heavy precipitate of the mixed colouring matters is eventually produced. To within recent years this reaction was carried out on a commercial scale, and the product was placed on the market under the name of 'rhamné-tine.' This reaction can be employed to distinguish between the dyeing properties of the glucosides contained in the berries, and the free colouring matters produced by their hydrolysis. Thus if Persian berries be added to a cold dye-bath, and this is slowly heated to boiling, the glucosides are hydrolysed by the ferment; but if, on the other hand, the berries be at once plunged into boiling water, the ferment is destroyed, and the glucosides are obtained. Wool mordanted with tin gives an orange-red shade, whereas in the latter a pure yellow colour is produced.

Beyond the ordinary extract of Persian

berries which is prepared in large quantity by extracting the berries with boiling water, and evaporating the solution under reduced pressure, no special commercial preparations are manufactured at the present time.

**Dyeing properties.**—In wool dyeing Persian berries are little employed on account of their expensive nature; moreover, they possess no special advantage over quercitron bark and old fustic. Persian berries, as a rule, give redder shades than quercitron bark, a fact which is to be explained as due to the hydrolysis of its glucosides by the ferment. The quercitron of quercitron bark is not accompanied by such a specific ferment, and consequently the shades given by this dyestuff are of a yellower character. With tin mordant Persian berries give bright yellows and oranges, which are only fairly fast to light; but according to Hummel, the yellowish-olive produced with iron mordant is extremely fast, and is more so than otherwise by exposure. Persian berries are still used to a considerable extent in calico-printing for the formation of yellow, orange, and green shades.

A. G. P.

**PERSIAN GREEN.** *Emerald green v.*

**PIGMENTS.**

**PERSIAN RED.** *Basic lead chromate v. CHROMIUM.*

**PERSIMMON**, the fruit of *Diospyros virginiana* (Linn.), much cultivated in Japan, and now in California and other warm countries. When freshly gathered, the fruit has a very astringent taste, which it loses on keeping, especially if exposed to a low temperature.

König gives as its average composition—

	Invert	Cane	Other N-
Water	Protein	sugar	sugar
56.1	0.8	13.5	1.0
		16.0	1.8
			0.9

Tannin is abundant in the freshly gathered fruit, but on storage is deposited in an insoluble form, in certain specialised cells (Bigelow, Gore and Howard, J. Amer. Chem. Soc. 1906, 28, 688).

H. I.

**PERSULPHURIC ACID and PERSULPHATES v. SULPHUR.**

**PERTHITE v. FELSPAR.**

**PERU BALSAM v. BALSAMS.**

**PERUVIAN BARK v. VEGETO-ALKALOIDS.**

**PERYLENE** (*peri*-dinaphthylene). A hydrocarbon  $C_{20}H_{12}$  obtained by heating either naphthalene, or 1:1'-dinaphthyl with aluminium chloride; or by heating 1:8-di-iodonaphthalene with finely divided copper. Glistening yellow crystalline leaflets, m.p. 264°–265°, forming yellow to reddish-yellow solutions with a blue fluorescence (Scholl, Seer and Weitzenböck, Ber. 1910, 43, 2202).

**PETALITE.** A lithium aluminium silicate  $LiAl(Si_2O_6)_2$  containing 4.9 p.c. lithia, and much resembling spodumene [ $LiAl(SiO_3)_2$ ] in appearance. It usually forms platy, cleavable masses (hence the name, from *πέταλον*, a leaf) of a white, grey, or pinkish colour and with a vitreous lustre; sp.gr. 2.4 (that of spodumene being 3.16). It is found, together with other lithium-bearing minerals (lepidolite, tourmaline, and spodumene), in an iron mine on the island of Utö near Stockholm, where it has been mined as a source of lithium salts. It was in this mineral that lithium was discovered by J. A. Arfvedson in 1817. Other localities are Peru in

Maine, and Bolton in Massachusetts. A colourless, glassy variety, known as castorite, is found in the granite of the island of Elba. L. J. S.

#### PETIT-GRAIN OIL v. OILS, ESSENTIAL.

**PETROFRACTEUR.** An explosive resembling *kieselite* (v. EXPLOSIVES) in composition, but differing specially in that it contains no gun-cotton. Is said to consist of a mixture of 10 p.c. nitrobenzene, 57 p.c. potassium chlorate, 20 p.c. potassium nitrate, and 3 p.c. antimony pentasulphide (v. Watson Smith, J. Soc. Chem. Ind. 1887, 5).

#### PETROLEUM.

##### AMERICAN PETROLEUM.

##### 1. Occurrence.

Three closely-related raw materials, all belonging to the class of bitumens, have been noted as occurring associated together, sometimes as distinct occurrences, sometimes in complete physical admixture, viz. natural gas, liquid petroleum, and ozokerite or natural paraffin. To these three must be added, in considering the American production, a fourth variety of bitumen, asphalt, for we have learned to speak of petroleum with a paraffin base and petroleum with an asphaltic base, from which latter variety much true asphalt can be and is now industrially obtained.

Leaving this distinction between native petroleum to be referred to more fully in speaking of the ultimate products and utilisations, we will note the present production of crude petroleum in America. The producing fields are now commonly grouped under eight heads: (a) the Appalachian field, (b) the Lima-Indiana field, (c) the Illinois field, (d) the Mid-continent field, (e) the Gulf field, (f) the California field, (g) other fields of the United States, (h) Canadian field.

**The Appalachian field.** Under this head is now included the production of Pennsylvania, New York, Eastern Ohio, West Virginia, Kentucky and Tennessee, which states lie along the Appalachian range. In general, the oil is what is known as 'Pennsylvania' grade, and commands a higher price than any other. This is because it contains a paraffin base, is practically free from sulphur compounds, and, in consequence, is more readily refined and yields a higher percentage of valuable products. In certain parts of this field very valuable natural lubricating oils are obtained, and in some amorphous paraffin separates out in the tanks used for storage of the crude oil and in the pipe-lines. Because this petroleum is so largely made up of the paraffin series of hydrocarbons, it is easily refined by acid treatment and yields the largest proportion of gasoline and burning oil. It is true that the Kentucky and Tennessee oils are not quite equal to the Pennsylvania grade, but they are nevertheless of the same paraffin-base class of oils. Of the states comprising the Appalachian field, West Virginia now leads, second, and south-eastern Kentucky third. In this grade of crude oil is gathered by the pipe-lines under collective names of Bradford crude in the northern part, Middle-District crude for the central, and South-Western crude for the West Virginia and South-Eastern Ohio oil.

**The Lima-Indiana field.** This takes its name

primarily from the town of Lima in Northern Ohio where this class of oil was first produced. It does not come from a sandstone formation as in the case of the Appalachian oil, but from what is known geologically as the Trenton limestone, in which alteration of the dolomitic limestone has left porosity sufficient for considerable oil accumulations. This oil, as that from the neighbouring state of Indiana, is sulphur containing, and therefore more difficult and expensive to refine. It, however, contains a paraffin base, and is now made to yield products nearly or quite equal to those obtained from Pennsylvania oil.

**The Illinois field.** This is of relatively recent development, only having begun to produce in 1899, but in 1909, it ranked third in amount of production, being exceeded only by California and the mid-continent fields. It now exceeds the entire Appalachian field in its production.

The oil is in the main found in the sandstone formation, and hence is less sulphurous than that from the Lima-Indiana field. It is also a paraffin-base oil, and as far as examined chemically it seems to stand intermediate between the Pennsylvania oils and the Lima-Indiana oil.

**Mid-Continent field.** The area included in this field consists of southern Kansas, the oil deposits of the new state of Oklahoma (formerly Indian territory), and northern Texas. This field is also of comparatively recent development, having developed from less than one million barrels in 1902 to about fifty million barrels in 1909, and 53,500,000 barrels in 1910, so that it is only exceeded in production at present by the California field. By far the largest amount of the oil is produced in Oklahoma, Kansas coming second. The oil is most generally of a somewhat asphaltic base, although paraffin-containing oil is obtained from part of the field. Very much of the oil from this field is now used as fuel oil and has been extensively introduced in place of coal, so that the production of the latter has fallen off in several of the states supplied by pipe-line from the Oklahoma oil regions.

**The Gulf field.** This includes the oil fields of Louisiana and coastal Texas. In this field, the accumulation of petroleum is determined by a type of geologic structure which is unique. The oil occurs in recent rocks and these formations are characterised by flat or gently sloping strata, in which occur peculiar domes. These latter are probably produced, perhaps due to subterranean pressure, of salt, gypsum and limestone, which may have elevated the strata above them so as to form these characteristic domes or 'mounds,' as they are called. Drilling on the top or sides of these domes has developed, as at Spindletop,

associated with salt water. Most of the Texas oil is mainly valuable for fuel oil, because of the low percentage of burning-oil fraction obtainable and the presence of heavy hydrocarbons. It, moreover, is largely of an asphaltic base, and therefore the residuums from Texas oils have been of especial value for fluxing the hard asphalts. The Beaumont oil is one of the strongest in sulphur of American petroleum and the sulphur compounds are of an unstable character so that free sulphur at times deposits

from them, as was first established by Richardson, and in their distillation much hydrogen sulphide is liberated.

*The California field.* This field, since 1909, has become the first in amount of production, having furnished in that year the enormous yield of 58,250,300 barrels, and in 1910 the still larger production of nearly 78,000,000 barrels.

The California production is moreover practically all obtained from four or five contiguous counties in southern California, partly coastal and partly forming the valleys between the Sierras and the Coast Range. Kern and Fresno counties, which lie inland, are at present the most prolific sections, the noted Coalinga deposit being in the latter county, while Santa Barbara, Ventura, and Los Angeles counties, which are coastal counties, are next in importance. The California oil sands have been found to be of much greater thickness than those of eastern fields. In some instances 1100 feet of oil sand has been encountered in a well and in hundreds of wells from 200 to 500 feet of sand are found. This insures a long life to the individual wells. While there is some variation in the California oils, they are in general distinguished by two characteristics: they almost all contain nitrogen, indicating in part at least an animal origin, and they contain more sulphur than a paraffin base. Indeed, the residue associated with solid asphalt is of the residuum from California as asphaltic flux and for the manufacture of artificial asphalt. Much of the California oil is used as fuel oil, and enormous quantities are taken for this purpose by the railroads and steamship lines.

*Other fields of the United States.* Only two additional states require special mention in this connection, Colorado and Wyoming. Colorado for a number of years has produced a moderate amount of an oil with a paraffin base and free from sulphur, the production being centred in two localities, Florence and Boulder. Wyoming produces an oil, also free from sulphur, and especially characterised by the excellent quality of the lubricating fraction so that it has commanded a special price.

## II. Physical and Chemical Properties.

The petroleum of North America as now known differ very widely in both physical and chemical characters. When the American petroleum industry began in 1861, and for many years thereafter, the oil that was refined and marketed was Pennsylvania crude, or as it is now called, "Rocky Mountain oil." This, as already stated, is a paraffin base oil and yields a large percentage of high quality burning oil and paraffin, and is substantially free from sulphur and nitrogen. Later the Lima, Ohio oil, and the Canadian oils were discovered, which contained a smaller percentage of illuminants and notable amounts of sulphur compounds and required a special and more expensive refining treatment. They, however, contained a paraffin base. The California oil, however, was of notably different type, much of it was very heavy, some being found of a density as low as 12°B., and it yielded very little illuminating oil. It was soon found to contain, in addition to sulphur, organic nitrogen com-

pounds, and the hydrocarbons present were not of the paraffin series, which were so characteristic of Pennsylvania oil, but heavy asphaltic oils which, on concentration, yielded solid asphalt material.

The Texas oil, which next appeared, seems in large degree to be intermediate between these types, and while yielding some paraffin contains also much asphaltic base. It is also specially characterised in some localities by an abundance of free sulphur, and even free sulphur. The Texas oil, as already stated, is more an approximation to the Appalachian field, yielding a paraffin-base oil, although with more sulphur than Pennsylvania oil, while the Mid-Continent field, on the other hand, yields predominantly an asphaltic-base oil, although yielding paraffin in many cases.

The crude petroleum vary in colour and gravity from the dense California oils, which are almost black, to the light crudes, of 51°B. in parts of the Appalachian field, which are almost colorless in bulk and reddish-brown in color, or exceptionally yellow or amber in colour.

Scientific study of American petroleum has been made chiefly by Warren, C. F. Mabery, Clifford Richardson, and Young.

Besides the saturated paraffin series



which constitutes the bulk of the Pennsylvania oil, unsaturated open-chain hydrocarbons, probably of the series  $C_nH_{2n}$ , are found. The well-known aromatic series  $C_nH_{n-6}$  also occurs in many of the paraffin-base oils of Pennsylvania and Ohio, and in the asphaltic oil of California, but not, so far as known, in the Canadian oil or the Texas oils.

Saturated cyclic hydrocarbons of the series  $C_nH_{2n}$  and  $C_nH_{2n-2}$  and cyclic and not open-chain hydrocarbons have been recognised by both Mabery and Richardson as present in the heavier fractions of many oils both of the Pennsylvania and the California type.

Unsaturated cyclic hydrocarbons of high molecular weight are characteristic constituents of asphalt-base oils like those of California.

The sulphur compounds of the Lima and the Canadian oils are now believed by Mabery to be cyclic in character and to be methylene derivatives. He terms them "cyclic methylene derivatives." The nitrogen compounds of the California oils are basic bodies, and are supposed to be pyridine and quinoline derivatives.

Phenolic bodies have also been recognised in the California petroleum, and have been extracted in crystalline form by Richardson.

## III. Production and Transportation of the Crude Petroleum.

The oil comes from depths which vary within very wide limits according to the geological formations, from the heavy oil strata of West Virginia and Ohio, which are from 50 to 60 feet deep, to the producing strata of the Washington Co., Pennsylvania district, which are from 2400 to 2600 feet in depth, and to some of the California wells, where, as in the Santa Maria district, wells have been drilled to a depth of over 4000 feet. Many wells, particularly in newly-opened



oil and other products. A considerable quantity of crude petroleum, however, is exported from the United States to France to be refined there, the French duty on the refined oil encouraging the home refining.

The shipment of refined oil for the Far East is chiefly in cans of tin, two of which latter, holding five gallons American, or nearly four imperial gallons each, are packed together in a wooden case. These cases go to China, Japan, and warm climates, as the loss by leakage is less than when the barrel is used. The shipment of oil in bulk for the voyage across the Atlantic to Europe is now carried on most largely in tank steamers, and quite a fleet run from Philadelphia and New York to English and German ports. The most important feature of their construction is the provision of auxiliary tanks above the level of the main storage tanks and in communication with them. The storage tanks can thus always be kept full of oil, the auxiliary tanks serving to hold the surplus when the storage tanks become heated and supplying the deficiency when contraction takes place.

#### IV. Processes of Refining and Manufacture.

As petroleum has been shown to be a mixture of hydrocarbons of different volatility, the first operation would naturally be to effect a partial separation of these hydrocarbons by a process of fractional distillation. But, in fact, simpler lines of treatment were first tried. It was found that crude oils spread out over warm water in tanks and exposed to the sun were much improved in gravity and consistency. This process was chiefly employed for the production of lubricating oils, and the products were called 'sunned oils.' This was followed by the application of methods of partial evaporation or concentration in stills, either by direct application of heat or by the use of steam-coils, careful *refining* over-heating. The products were 'refined oils,' and form the best material for the manufacture of high-grade lubricating oils. They will be referred to again. The process to which the great bulk of crude petroleum is submitted, however, is that of fractional distillation, continued to the eventual coking of the residue. As the most valuable of the several distillates is that which is to be used

for illuminating oil, the percentage of that is an important item in an oil refinery. A normally conducted fractional distillation of Pennsylvania petroleum will give from 35 to 50 p.c. of oil suitable for illuminating purposes, and from 20 to 30 p.c. of lubricating oils. About 1865, however, it was found that if during the distillation the heavy vapours were made to drop back upon the hot oil in the still they became superheated and were decomposed. This process of destructive distillation or 'cracking' allowed of a notable increase of the illuminating oil fraction at the expense of the lubricating oil. So, at present, some 75-80 p.c. of burning oil is obtained, whilst the residuum from which the lubricating oil is obtained is reduced to 6 p.c.

The process of refining crude petroleum is generally divided into two quite distinct parts. The 'benzene' and burning oil distillate are run from the same still, when the fluid residuum is transferred to what are usually called 'tar

stills,' in which the rest of the distilling operation is conducted. The *benzene* still is in almost exclusive use at present, consist of a cylinder of boiler-plate, the lower half being generally of steel, 30 feet in length by 12 feet 6 inches in diameter. This still is set horizontally in a furnace of brickwork usually so constructed that the upper half of the still is exposed to the air, which facilitates the cracking in the latter part of the distillation. The working charge of the cylinder stills is usually 750 barrels, although 1000 barrels stills are often used. The stills are usually provided with steam pipes both closed and perforated. The steam issuing in jets from the perforated pipe has been found to facilitate distillation by carrying over mechanically the oil vapours.

The condensing apparatus varies somewhat in the details of its construction, but consists essentially of long coils of pipe immersed in tanks through which water is kept flowing. The terminal portions of the condensing pipes all converge and enter the receiving house within a few inches of each other. Near the extremity of each a trap in the pipe is made for the purpose of carrying away the uncondensable vapour. This may be allowed to escape or may be burned underneath the boilers or stills, effecting thereby a large saving in fuel. The condensing pipes generally deliver into box-like receptacles with plate-glass sides, through which the running of the distillate can be observed, and from which test portions can be taken from time to time for the proper control of the process.

The tar-stills are usually of steel, cylindrical in shape, holding about 260 barrels, and are set in groups of two or more, surrounded by brick-work. Vacuum-stills have been and are still used to some extent, especially in the preparation of reduced oils, for the manufacture of lubricants and products like vaseline. Of course, the evaporation in these stills takes place rapidly, and at the lowest temperature possible, insuring a fractional distillation and not a decomposition. If superheated steam be used, moreover, instead of direct firing, it is possible to reduce oils to 18° B. without any production of pyrogenic products. Continuous distillation has not proved commercially successful in the United States, but has latterly been taken up again and is used on certain kinds of crude oil.

To recur now to the products of the first rough distillation of crude oil, the first fraction, known as the 'benzene distillate,' is redistilled by steam heat in cylindrical stills holding 500 barrels, and is sometimes separated into the following products: cymogen, 100°-110° B. gravity; rhigolene, 90°-100° B.; gasolene, 80°-90° B.; naphtha, 70°-76° B.; benzene, 62° B. gravity. The time occupied in working the charge is about 48 hours. The deodorisation of the benzene, which is to be used for solvent purposes in pharmacy or the arts, is effected by the use of sulphuric acid, as in the treatment of the burning oil fraction, only the proportion of acid used is much smaller, and the agitation is effected by revolving paddles instead of by an air-blast. One-half of 1 p.c. is sufficient in this case. Other processes have been proposed for the deodorisation, such as the method of the United States Pharmacopoeia for 'purified

benzene, which is to agitate the benzene first with dilute sulphuric acid to which potassium permanganate has been added, and then with a solution to which a similar addition of potassium permanganate has been made, and followed finally by washing with water.

The treatment of the illuminating oil fraction is a more important process. It is first subjected to treatment with sulphuric acid, washing with water and a solution of caustic soda. This operation is conducted in tall cylindrical tanks of wrought iron, lined with sheet lead, which are called 'agitators.' The bottom is funnel-shaped, terminating in a pipe furnished with a stop-cock for drawing off the refuse acid and soda washings. The distillate to be treated must be cooled to at least 60°F., and before the main body of the acid is added for the treatment any water present must be carefully withdrawn. This is done by starting the agitation of the oil by the air-pump and introducing a small quantity of acid. This is allowed to settle and withdrawn. The oil is now agitated and about one-half of the charge of acid is introduced gradually from above. The agitation is now to be continued as long as action is indicated by rise of temperature, when the dark 'sludge acid' is allowed to settle and withdrawn. The remaining portion of the acid is added and the agitation takes place. The amount of acid needed for an average distillate is about 1½–2 p.c., or about 6 lbs. of acid to the barrel of oil. The acid as drawn off is dark-blue or reddish-brown in colour, and is charged with the sulpho-compounds of the olefines and other unsaturated hydrocarbons, while the free sulphur dioxide escapes in abundance. The oil, after treatment, consists of the paraffin hydrocarbons largely freed from admixture with olefines and other hydrocarbons. Its colour it has been changed to a very light straw colour. It is now washed with water introduced through a perforated pipe running round the upper circumference of the tank. This water percolates through the body of the oil, removes the acid, and is allowed to escape in a constant stream from the bottom.

When the wash-water shows no appreciable acid taste or reaction the washing is stopped and about 1 p.c. of a caustic soda solution of 12°B. is introduced and the oil is again agitated. When this is drawn off the oil is ready for the settling tanks. Washing with water after the soda treatment sometimes follows, but is not general. The settling tanks are shallow tanks, exposed to air and light on the sides, and in these any water contained in the oil settles out and the oil becomes clear and brilliant. The tanks are provided with steam coils for gently warming the oil in cold weather to facilitate this separation. The bringing of the burning oil fractions to proper fire-test is now always accomplished by 'steam-stilling,' or taking out until test is reached. These light vapours are of course condensed and go into the gasoline tank.

In the refining of the Canadian oil which contains sulphur impurities, after the caustic soda washing, the oil has been treated with a solution of litharge in caustic soda, agitation

being continued for about 6 hours, or until the oil is deodorised. Sublimed sulphur is then added and the agitation renewed. After the first drawing off a solution the oil is bleached in oil, however, is not freed from all its sulphur impurity, even by this elaborate treatment. More recently it has been found that distillation over finely-divided metallic copper under certain conditions will much more effectually free these oils from the sulphur, and this method has been extensively used in refining Lima Ohio oil.

The residuum of the original crude oil distillation is, as was said, distilled from the 'tar stills.' The first runnings, constituting from 20 to 25 p.c., will have a gravity of 38°B., and are returned to the crude-oil tank for distillation or are treated and purified as burning oil. The paraffin oil which now runs over may be caught in separate lots, as it deepens in colour and increases in density, or it may be all received together to be treated in the paraffin agitator with acid and purified for the separation of paraffin wax. The agitator in this case must be provided with steam pipes so that its contents can be kept perfectly liquid, and the charge of acid is larger, amounting to 3, 4, or even 5 p.c. The treatment included the usual washing with water and soda, all at the proper temperature. The 'sludge' becomes quite solid on standing, and is not worked over. After settling, the paraffin oil goes to the chill rooms, where, by the aid of the filtering machines and the circular filters, the whole is brought to a solid condition. The solid is then broken up, and the temperatures, and the oil is collected and may be broken up and then submitted to still greater pressure at a higher temperature (70°F.) than before, when it is known as 'refined wax.' To convert it into block paraffin it must be washed with benzene, pressed, melted, and passed through collected filtering clay, when it is colourless and solidifying to a hard translucent block.

The distillation of residuum is continued until the bottom of the still becomes red hot, when yellow vapours issue from the tail-pipe and a dense resinous product of a light yellow colour and nearly solid consistency distils over. This 'yellow wax' contains anthracene and other higher pyrogenic hydrocarbons. Its only use at present is to add it to paraffin oil to increase density and lower cold tests. The coke remaining in the still amounts to about 12 p.c. Reduced oils, obtained by careful driving off of the light fractions of the crude petroleum without cracking, as stated before, are of great value as lubricants. They are generally made by vacuum distillation, and the use of superheated steam instead of direct firing. They are either brought into the market at once without further treatment or after a bone-black or clay filtration. This production of filtered oils is usually combined with the manufacture of vaseline or 'petrolatum,' as it is now known in the U. S. Pharmacopœia. Taking a vacuum residuum as the raw material, this is melted and run on to filters of fine granular well-dried bone-black. The filters are either steam-jacketed or are placed in rooms heated by steam coils to 120°F.

or higher. The first runnings are colourless; and all up to a certain grade of colour go to the manufacture of vaseline. Beyond that the filtrate is known as 'filtered cylinder oil,' and is used as lubricant exclusively.

The process of filtration of oils through fuller's earth, now extensively practised with lubricating oils and paraffin, has also been applied in an experimental way by Dr. David T. Day, of the U.S. Geological Survey to crude petroleum with interesting results, showing not only a decolourising effect, but in addition a fractionation. These results are briefly summarised thus (Bulletin, 365, U.S. Geological Survey): '1. When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom. 2. When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards when more water is added. 3. When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffin hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom. 4. When oil is displaced by water, about one-third of the oil remains in the earth.' These results are interesting, as throwing light upon the occurrences of different grades of crude oil under different geological conditions.

There are several relatively new lines of manufacture of petroleum products that also require special mention.

The great demand for gasoline for automobile, motor-boat, and manufacturing processes has caused petroleum refiners to turn to all possible sources of it. In California, for example, normally 100 barrels of crude oil yield 20 barrels of a good quality gasoline, and the production of gasoline has now risen to 200 barrels per year. Much attention has been given to obtaining a light gasoline by condensing the heavier portions of natural gas, especially what is termed 'casing-head gas.' In West Virginia and south-eastern Ohio several plants have been started for condensing from this gas its liquefiable portions. Gas-pumps are in use for drawing from petroleum wells the heavier portions of the petroleum gas, much of which is condensable. In California large quantities of heavy petroleum gas are also obtained, and it is stated that every 1000 feet of the gas will yield, on condensation, two gallons of gasolene. As thousands of irrigating plants are driven by gasolene engines, and many gas motors are in use for all kinds of work, the demand for gasolene has made this new source a very welcome one.

Gas oils are now produced extensively from such crude petroleum, which distillates at a higher temperature than gasoline, and are used for power, and is mixed with kerosene, which, although cheap, has no value unless carburetted.

Petroleum residuums, notably the Lima residuum and latterly the Mid-Continent oil residuums, are blown with a current of air, while kept at a temperature below their distilling-

point, with the result of the formation of a semi-solid or solid product resembling asphalt and used at present extensively as a flux for the hard natural asphalts. The California petroleum readily yields a residue when distilled and mu... for paving purposes is made in this state. Sulphur, when heated with the liquid California petroleum of asphaltic base, also causes a thickening and the production of a solid asphaltic flux.

#### V. Character of Products and Utilisations.

The names of commercial products obtained from petroleum have, of course, been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally accepted classes of products. The first fraction commercially obtained is the 'light petroleum.' This may be obtained by distillation and proper condensation:—

*Cymogene*, gaseous at ordinary temperatures, but liquefiable by cold or pressure, b.p. 0°C., sp.gr. 110°B. Used in the manufacture of ice.

*Rhigolene*, condensable by the use of ice and salt, b.p. 18.3°C., sp.gr. 0.60 or 100°B. Used as an anæsthetic for medical purposes.

*Light Petroleum or P.* b.p. 70°–90°C., sp.gr. 0.650–0.666 or 85°–80°B. Used as a solvent for caoutchouc, asphalts, and fatty oils, and for carburetting air in gas machines.

The light petroleum used by chemists for solvent purposes may be very light, 88°B., or may be as heavy as 62°B., which latter is used in certain classes of extraction.

*Ligroin* is another name for light petroleum.

*Benzine* (deodorised), sp.gr. 0.638–0.660 at 25°C. (82°–89°B.), boiling at 45°–60°C., is the light solvent described in the U.S. Pharmacopœia.

*Gasoline*. This term is applied to the product used for motor-boats, and internal-combustion engines, and because of its demand may vary quite widely in quality. More recently, gasoline has been made now not only from natural gas, but from oils like California, which are differently constituted, and the products will differ quite in characters. Thus a California gasoline will evaporate at ordinary temperatures much more readily than Pennsylvania gasoline reading 80°B. or higher. Or again a well-made 60°–63° gravity naphtha, manufactured from Mid-Continent crude, has a lower b.p. than 76° gravity naphtha made from Pennsylvania crude.

In general, commercial gasolines are of heavier gravity than before the demand grew to its present figures.

*Burning oil or kerosene*. The different burning oils are known often by special names, of which the number is legion, but they are graded by the American petroleum exporters, chiefly according to the two standards of colour and fire-test, the colours ranging from pale-yellow (standard-white) to straw-coloured, and colourless (water-white). The oils, of which the commercial oils are mostly brought are 110°F., 120°F., and 150°F., that of 110° going mainly to the Continent of Europe and to China and Japan, and that of 120° to England.



Most of the kerosene for export is now refined on the basis of the Abel test. An oil of 150°F. fire-test and water-white in colour is known in the trade as 'head-light oil.' An oil of 300° fire-test, and sp.gr. 0.829 is known as 'mineral sperm' or 'mineral-colza' oil.

*Lubricating oils* from petroleum have assumed an importance which is increasing every year. Some crude petroleums like those of Franklin and Smith's Ferry, Pennsylvania, Mecca, Ohio, Volcano, W. Virginia, and other localities, are natural lubricating oils, requiring little or no treatment to fit them for use. The other petroleum lubricating oils are prepared in one of two ways—either by driving off the light hydrocarbons from the crude oil, yielding what is called a 'reduced oil,' or they are the oils obtained by distilling the petroleum residuum in tar-stills. The lightest of the lubricating oils, varying in gravity from 32°B. to 38°B., are frequently called 'neutral oils.' They are largely used for the purpose of mixing with animal or vegetable oils, and it is therefore necessary that they should be thoroughly deodorised, decolourised, and deprived of the blue fluorescence or 'bloom.' The first two results are accomplished by bone-black filtration, the last in various ways, such as treatment with nitric acid, addition of small quantities of

... oils are called 'spindle' S. P. S.

#### PETROLEUM FROM OTHER SOURCES THAN AMERICA.

Towards the close of the nineteenth century the United States and Russia occupied positions of great importance in respect of the present and future production of petroleum than is now known. In recent years there has been great activity in the exploration of petrolierous regions and the exploitation of other sources of supply, with the result that, although the United States furnishes considerably more than half the aggregate output, many other countries are now contributing on a scale of increasing commercial importance, and the production of petroleum has become widespread in character.

In these circumstances it is desirable to give statistics of the production of petroleum for 1911, the latest for which official returns are available. In order to supplement the account of the petroleum industry in the United States by particulars of the corresponding industry in other countries (see to)

#### Russia.

There can be little doubt that the so-called Eternal Fires at Surakhani, on the Apsheron peninsula, have been frequented by fire-worshippers since the commencement of the Zoroastrian period, to which the date of 600 B.C. has usually been assigned, although the temple which now stands in that locality is considered to be of Hindu origin, and is probably not more than two centuries old.<sup>1</sup> In Gibbon's

#### WORLD'S PRODUCTION OF CRUDE PETROLEUM IN 1911. (Day.)

Source.	Metric Tons.	Percentage of Total.
United States	29,393,252	63.80
Russia	9,066,259	19.16
Mexico	1,873,522	4.07
Dutch East Indies	1,670,668	3.52
Roumania	1,544,072	3.21
Galicia	1,458,275	3.04
India	897,184	1.87
Japan	221,187	0.48
Peru	186,405	0.40
Germany	140,000	0.29
Canada	38,813	0.08
Italy	10,000	0.02
Other Countries*	26,667	0.06
	46,526,334	100.00

\* Estimated.

'Decline and Fall of the Roman Empire' it is recorded that Heraclius, having, in A.D. 624, wintered in the Mogan Steppes, at the mouth of the river Kura, 70 miles south of Baku, 'signalised the zeal and revenge of a Christian Emperor. At his command, the soldiers extinguished the fire and destroyed the temple of the Magi.'

Marco Polo, writing in the thirteenth century, says, 'On the confines towards Georgine, there is a fountain from which oil springs in great abundance, inasmuch as a hundred shiploads might be taken from it at one time. This oil is not good to use with food, but 'tis good to burn, and is also used to anoint camels that have the mange. People come from vast distances to fetch it, for in all the countries round there is no other oil.'<sup>1</sup> With reference to this, Colonel Yule remarks, 'Though Mr. Khanikoff (the celebrated Russian traveller) points out that springs of naphtha are abundant in the vicinity of Tiflis, the mention of shiploads (in Ramusis, indeed, by the editor—to camel-load) quantities spoken of, point to the naphtha wells of the Baku peninsula on the Caspian. Ricold speaks of their supplying the whole country as far as Bagdad, and Barbaro speaks of their practice of anointing camels with oil.' Peter the Great, upon annexing Baku in 1723, made arrangements for the collection of the oil and its transportation up the Volga. A few years later, Baku having meanwhile been restored to Persia, attempts were made by England to establish a trade with India *via* the Caspian Sea, and, some complications having arisen, Mr. Jonas Hanway was deputed to proceed to Persia to investigate affairs. Upon his return Mr. Hanway published, in 1754, *An Account of British Trade over the Caspian Sea*, wherein the occurrences to petroleum occur: 'The Fire-worshippers, or Fire-worshippers, call this phenomenon of a very great devotion. This object of devotion lies about ten English miles north-east by east from the City of Baku, on a dry rocky land. There are several ancient temples built with stone, supposed to have been all dedicated to

<sup>1</sup> When the present writer visited Baku in 1884, he found this temple deserted, and the fires extinguished, but he had no difficulty in igniting the gas.

<sup>1</sup> The Book of Ser Marco Polo, the Venetian. Edited by Colonel Henry Yule, C.B., London, 1871.

fire. Amongst others is a little temple at which the Indians now worship. Here are generally forty or fifty of these poor devotees, who come on a pilgrimage from their own country. A little way from the temple is a low cleft of a rock, in which there is a horizontal gap, two feet from the ground, nearly six long, and about three broad, out of which issues a constant flame, in colour and gentleness not unlike a lamp that burns with spirits, only more pure. When the wind blows it rises sometimes eight feet high, but much lower in still weather. They do not perceive that the flame makes any impression on the rock. This also the Indians worship, and say it cannot be resisted, but if extinguished will rise in another place. The earth round the place, for above two miles, has this surprising property, that by taking up two or three inches of the surface and applying a live coal the part which is so uncovered immediately takes fire, almost before the coal touches the earth; the flame makes the oil hot, but does not consume it, nor affect what is near it with any degree of heat. Any quantity of this earth carried to another place does not produce this effect. Not long since eight horses were consumed by this fire, being under a roof where the surface of the ground was turned up, and by some accident took flame. If a cane or tube, even of paper, be set about two inches in the ground, confined and closed with earth below, and the top of it touched with a live coal, and blown . . . a flame issues without hurting . . . or paper, provided the edges be covered with clay; and this method they use for light in their houses, which have only the earth for the floor. Three or four of these lighted canes will boil water in a pot, and thus they dress their victuals. The flame may be . . . in the same manner as that of spirit . . . ground is dry and stony, and the more stony any particular part is, the stronger and clearer is the flame; it smells sulphurous, like naphtha, but not very offensive. Lime is burnt to great perfection by means of this phenomenon, the flame communicating itself to any distance where the earth is uncovered to receive it. The stones must be laid on one another, and in three days the lime is completed. Near this place brimstone is dug, and naphtha springs are found. Baku supplies Ghilan and Mazanderan and other countries contiguous with naphtha. Hanway adds that 'the chief place for the black or dark-grey naphtha' was 'the small island Wetoy, now uninhabited, except at such times as they take naphtha from thence.' The island thus referred to is Sviatoi or Holy Island, which lies at the extremity of the peninsula of Apsheron. Of the Wetoy naphtha Hanway says, 'The Persians load it in bulk in their wretched vessels, so that sometimes the sea is covered with it for leagues together. When the weather is thick and hazy, the springs boil up the higher, and the naphtha often takes fire on the surface of the earth, and runs in a flame into the sea in great quantities, to a distance almost incredible. In clear weather the springs do not boil up above two or three feet; in boiling over the oily substance makes so strong a consistency as by degrees to almost close the mouth of the spring. Sometimes it is quite closed, and forms hillocks

that look as black as pitch, but the spring which is resisted in one place breaks out in another. Some of the springs which have not been long open form a mouth of eight or ten feet diameter. The people carry the naphtha by troughs into pits or reservoirs, drawing it off from one to another, leaving in the first reservoir the water or the heavier part with which it is mixed when it issues from the spring. It is unpleasant to the smell, and used mostly among the poorer sort of the Persians and other neighbouring people, as we use oil in lamps, or to boil their victuals; but it communicates a disagreeable taste. They find it burns best with a small admixture of ashes. As they obtain it in great abundance, every family is well supplied. They keep it at a small distance from their houses, in earthen vessels underground, to prevent any accident from fire, of which it is extremely susceptible.' Hanway also describes a 'white' variety of . . . on the peninsula of Apsheron, as 'of a much thinner consistency than black naphtha. The Russians drink it both as a cordial and medicine; but it does not intoxicate. If taken internally it is said to be good for the stone, as also for disorders of the breast, and in venereal cases and sore heads; to both the last the Persians are very subject. Externally applied, it is of great use in scorbutic pains, gouts, cramps, &c., but it must be put to the part affected only; it penetrates instantaneously into the blood, and is apt, for a short time, to produce great pain. It has also the property of spirits of wine to take out greasy spots in silks or woollens, but the remedy is worse than the disease, for it leaves an abominable odour. They say it is carried into India as a great rarity, and being prepared as a japan is the most beautiful and lasting of any that has yet been found.' A third source of petroleum mentioned by Hanway is the island of Tcheloken on the eastern side of the Caspian. Of this island, on which at the present time great activity prevails in . . . Captain Woodroffe says, . . . came in close under the . . . as the Russians call it. The Persians call it Cherriken. The coast is difficult of access, being high. It contains about thirty-six families who have twenty-eight large boats, with several wells of naphtha. The people exist entirely by piracy. To remedy this evil Nadir Shah, some years ago, offered to forgive all that was past, and to receive them into his favour, if they would come and settle about Astrabad Bay, where they might have lands and sell their naphtha to the inhabitants of that quarter. This they accepted, and carried on a brisk trade for about two years, selling their naphtha to the Persians, Turkomans, &c.; but, getting tired of this way of living, returned to their trade of piracy.

Russia again annexed Baku in 1806, and the monopoly of the petroleum was conferred on a . . . of Mirzoeff, who held it until 1872, when the monopoly was revoked and a tax imposed.

The abolition of the . . . had the effect of greatly . . . and Mirzoeff did . . . position of supremacy, for in . . . Company struck a flowing well which yielded a large supply;

and in the following year the Transcaspian Trading Company, afterwards called the Baku Petroleum Company, took the lead in the business. In 1875 Messrs. Nobel Brothers commenced the systematic production, refining and transportation of petroleum upon a large scale, and by the introduction of approved appliances for drilling and refining, as well as by the installation of a complete system of pipelines, tank steamers, tank barges, tank railroad waggons, and storage tanks, inaugurated a new era in the Russian petroleum industry.

For many years these operations were confined to a few square miles in the Baku district, the producing fields including Balakhani, Sabuntchi, Romani, and Bibi-Eibat, but within this small area such prolific wells were drilled that a very large production was obtained. Thus the celebrated Drojba fountain, completed in 1883, commenced spouting at the rate of 1,600,000 to 2,000,000 gallons daily, valued at £11,000, and other wells drilled within later years have had for a time a daily yield of more than double that quantity.

In 1893 the Grozni field, which lies about 300 miles north-west of Baku, began to attract attention, and two years later it gave so productive a fountain that the outflowing oil converted a neighbouring valley into a vast lake in which large ships could have floated. From that time the progress of Grozni was rapid, and it now ranks as one of the great oilfields of Russia.

The oilfield of Maikop, in which a large amount of English capital has already been expended in drilling operations, is situated in the Kouban territory, about 300 miles west of Grozni. The early promise of large production from moderate depth given by the completion of prolific spouting wells has not been fulfilled, but new wells are being drilled. Meanwhile, however, a steady yield is being obtained from certain parts of the field. Other petroliferous lands lie still further to the north-west on the Taman Peninsula.

As already mentioned, the Island of Teheleken, on the eastern side of the Caspian Sea, is now being actively exploited with the drill, and spouting wells have been obtained. Ozokerite is also being obtained here in commercial quantity.

Another district in which spouting wells have recently been obtained by drilling is that of Gurieff, in the province of Uralsk, on the northern side of the Caspian Sea.

The cable system of drilling, commonly employed in the United States, which has already been described, has not found favour in Russia, although it has been used. The method adopted is, however, substantially similar, in the sense that the strata are perforated by rapidly successive blows of a steel bit, or cutting chisel, suspended from the end of an oscillating beam, but the drilling tools are attached to the beam by a string of screw-jointed iron rods, added to as the depth of the well increases, instead of being suspended by a Manila cable, as in America. As the drilling progresses, the detritus is, from time to time, removed from the bore-hole by means of a long cylindrical vessel with a foot-valve, as in the American system. The well is also similarly lined with iron casing, but, owing

to the large diameter, riveted casing is used in place of screwed artesian casing. The greater diameter of the Russian wells is due to the need for providing for the use of a bailer (valved cylinder) for raising the oil when the well does not flow, the oil containing so much sand that pumps cannot be used. To some extent the air-lift system of raising the oil has been substituted for bailing within recent years. Motive power for the drilling machinery is ordinarily supplied by a steam-engine, and it is customary to take the steam supply from a central generating station, but the internal combustion engine is also employed, and the use of electricity as a motive power is growing. The oil is transported to the refineries by means of pipe-lines, as in America, and is to some extent stored in similar iron or steel cylindrical tanks of large size, but earthen storage reservoirs are also largely used.

In the refining of the crude oil it is the practice to adopt the system of continuous distillation, which consists in causing the oil to flow through a connected series of horizontal stills heated to successively higher temperatures, each still being provided with a separate condenser, so that a series of distillates of progressively higher boiling-points is simultaneously obtained. In this respect the process of fractional distillation differs from that adopted in America. In the treatment of Baku petroleum the refiner aims at obtaining the largest yield of the *ostatki*, or residuum, for which there is a large sale as liquid fuel, the kerosene being a product of secondary importance, though a certain proportion of the residuum is further distilled for the manufacture of lubricating oils, as in America. The 'cracking' process, largely employed in the United States as a means of increasing the yield of kerosene, is not adopted in Russia, and in this respect also the procedure in the two countries differs. The yield of kerosene from the crude oil of the older Russian fields does not usually exceed 25-30 p.c., and in the manufacture of the lubricating oils there are no solid hydrocarbons to be separated in the form of paraffin wax, as in America; but oils are now being met with in the newer Russian fields which not only contain a far larger proportion of the more volatile hydrocarbons, but also a considerable percentage of solid hydrocarbons.

The crude petroleum of the Baku district has a specific gravity usually within the limits of 0.865 and 0.875. It is of dark-brown colour and not unpleasant odour. In chemical composition it differs from Pennsylvania and other United States oils in largely consisting of hydrocarbons of the  $C_nH_{2n}$  series, which belong not to the ethylene group, but to what is known as the naphthene, or  $C_nH_{2n-6}+H_6$ , group.

The yield of benzene from the oil of the Balakhani-Sabuntchi field is very small, but a larger proportion of this product is obtained from the Bibi-Eibat oil. The kerosene ordinarily has a specific gravity of about 0.825, which is considerably higher than that of the parallel United States product. Of residuum (*ostatki*), or fuel oil, with a specific gravity of about 0.912, the yield is from 50 to 60 p.c. The flash-point of this fuel oil is about 140°F., and its calorific value is 10,800 calories, or

19,440 B.T.U. The comparatively small proportion of the residuum which is subjected to further distillation for the manufacture of lubricating oils yields first an intermediate product, known as solar oil, which is largely used as a source of gas for illuminating purposes. About 30 p.c. of the residuum is represented by a machine oil of a specific gravity of about 0.908, and of fairly high viscosity, which is an excellent lubricant for general use.

The crude petroleum of the Grozni field is of higher specific gravity than that of the Baku region, but contains a larger proportion of the more volatile constituents.

For consumption in Russia the kerosene is conveyed from the Baku refineries in bulk by tank-steamers to the mouth of the Volga, and thence by tank-barges and railway tank-waggon. For shipment abroad the kerosene was formerly transported to Batoum by railway tank-waggon, but within recent years a pipeline for the conveyance of it to the Black Sea has been in operation.

#### *Austria-Hungary.*

**Galicia.** The petroleum industry of Galicia is one of considerable antiquity, for the oldest historical records show that the oil was collected for use as cartgrease from very early times, and as a medicinal agent Galician petroleum was held in high repute, under the name of 'earth balsam,' as far back as 1506. In 1810, or between that year and 1818, oil from the Drohobycz district is said to have been distilled by Hecker and Mitis in a small refinery at Kabcza, and the product is reported to have been used for lighting the Alstetter in Prague. Refining does not, however, appear to have been generally practised until 1852, when a manufacturer of cartgrease named Schreiner took some of the liquid condensed on the cover of a vessel in which he had heated the crude oil to an apothecary of the name of Mikolaseh, whose assistants, Lukasiewicz and Zeh, treated the distillate with sulphuric acid and caustic soda, and obtained a burning oil of such excellence that renewed attention was directed to the subject. In the following year Galician petroleum replaced candles for lighting the station of the Emperor Ferdinand's North Railway, and in 1854 it obtained a footing as an article of commerce in Vienna.

The Galician oil-deposits extend for a length of about 220 miles, with a width of 40 to 60 miles, in a general north-westerly and south-easterly direction along the northern slopes of the Carpathian mountains. The unexploited deposits in Bukowina and in Transylvania, and the highly important and rapidly developing oil-fields of Roumania, occupying the south-eastern and southern slopes of the Southern Carpathians or Transylvanian Alps, may be regarded as an extension of the Galician deposits.

The earliest systematic exploitation of the petroliferous lands of Galicia was commenced in 1854 in the Bobrka district, between Krosno and Dukla; but the wells were merely shallow hand-dug shafts, which yielded no great quantity of oil, and it was not until many years later, when drilling by steam-power was adopted, that the production assumed commercial importance. To Messrs. Bergheim and MacGarvey

the credit is due of having laid the foundation of the present Galician petroleum industry by the introduction of the Canadian system of drilling in the year 1882. This system, which differs mainly from what is known as the American system in the use of wooden rods instead of a cable for the transmission of the drilling tools, it had proved to be for Canada, and for many years the only alteration made in it was to increase the weight of the tools; but latterly the much greater depth of the wells has led to the employment of a combination of the rod system with a wire-cable system. The chief centre of the petroleum industry of Galicia is the prolific field, which yields a very large proportion of the total output. Many of the wells here exceed 1000 metres in depth, and are costly to drill, but flowing freely, the oil is obtained, and the production is such that heavy expenditure in drilling is justified. The crude oil is of good quality, and yields all the usual commercial products, including paraffin wax.

The world's supplies of ozokerite are mainly obtained from the Boryslaw mines. The ozokerite deposit, which is unique in character, extends over a pear-shaped area, the richest part of which is only about 52 acres in extent, and is mined by means of shafts and drifts or galleries. It occurs in veins of varying thickness, and is mined by picks. The ozokerite is obtained partly in fragments of nearly pure material, but more largely in admixture with the matrix, from which it is separated by hand-picking or sorting and by the use of hot water, a further yield being obtained by the use of benzine as a solvent. The crude ozokerite, which is of dark greenish-brown colour, and about as hard as beeswax, is melted, cast into blocks, and delivered to the refineries, where it is treated with Nordhausen oil of vitriol and afterwards with charcoal. The purified and partly decolourised material, which is known as ceresin, has a m.p. of 61° to 78°, and is largely employed as an adulterant of, or even as a substitute for, beeswax in the manufacture of church candles. For the production of the substance of which ordinary candles of high melting-point are made, the crude ozokerite is subjected to distillation in a current of superheated steam, when about 60 p.c. of white wax of a m.p. of 140°F. is obtained. The by-products of the distillation consist of light oils and a semi-solid substance similar to vaseline, which, after purification, has been used by French perfumers as a substitute for lard in the process of *em-fleurage*. The residue in the stills consists of a hard, black, waxy substance, which when incorporated with indiarubber and subjected to vulcanisation, yields the product termed *okonite*, used in coating electrical cables. Okonite is not only a good insulator, but is remarkably flexible and tough. From the residue a 'heel-ball,' employed to impart a black polished surface to the heels and soles of boots, and to the leather-work of harness, is also made (*v. OZOKERITE*).

**Hungary.** The oil-fields of Hungary geologically resemble those of Galicia, but the petroliferous area on the Hungarian side of the Carpathian range is comparatively narrow, and

has not as yet assumed any great industrial importance.

#### *Roumania.*

As already stated, the petroliferous region of Roumania may be regarded as an extension of that of Galicia; it is also, doubtless, connected under the sea with that of the Caucasus. The Roumanian deposits may be traced by the outcrop from the Galician frontier to the Iron Gates, a distance of about 400 miles, and the width of the belt is from 15 to 20 miles.

The use of the 'liquid bitumen' of Roumania as a medicine, as an illuminating agent, and as a lubricant, was mentioned by the traveller Raicevich in 1750, but the existence of numerous pits and timbered hand-dug shafts of great age attests the fact that petroleum was systematically collected in the country long before that date. For many years after the introduction of drilling by steam-power in Galicia the petroleum of Roumania was still obtained in this primitive fashion, and the development of the industry was retarded, but similar methods are now adopted in both countries.

The expansion of the industry has been rapid, and bids fair to outstrip that of the corresponding industry in Galicia. The principal producing territories are in the districts of Prahova, Dimbovitza, Bacau, and Buzeu, and of these the first-named has hitherto been the most important.

The crude oil is of excellent quality, and in respect of the yield of the more volatile products occupies a position midway between those of Pennsylvania and Baku oils. The manufacture of fuel oil from the Roumanian crude petroleum is very largely carried on, although the residuum is also converted into lubricating oils to a considerable extent.

#### *Sumatra, Borneo, and Java.<sup>1</sup>*

**Sumatra.** The development of the oil-fields of Sumatra dates from 1885, when a flowing well was completed on a concession, granted two years previously, in Langkat, North Sumatra. In 1890 the Royal Dutch Company was formed to exploit another concession of oil-bearing lands in Langkat, and this company, besides drilling a number of wells during the ensuing five or six years, erected a refinery on the Bay of Aru, and laid a pipe-line to convey the crude oil from the wells to the refinery. The company also acquired and worked concessions in other districts, including Prah, in the Atchin Residency, and in the Palembang district. In 1897 the Petroleum Company was formed, and this company in the course of the next few years obtained a large yield in the Palembang district of oil of low specific gravity (0.765 to 0.775), for the transport of which a pipe-line was laid to a refinery erected on the river Lalang. In the same year (1897) a third company, the Moeara Enim Company, was formed, to work concessions on the River Enim and elsewhere in Palembang and drilled a large number of wells, many of which were 'spouters' yielding from 400 to 800 tons daily of oil of sp.gr. 0.792. This

company's refinery was built on the Musi, 3 miles below the town of Palembang, and the distillation of the crude oil was conducted on the continuous principle. In 1901 a fifth company, the Moesi Ilir Company, was added to the list, and commenced work on lands situated on the right bank of the Musi. The oil obtained here from spouting wells had a sp.gr. of 0.812 to 0.889. The company laid a pipe-line to Palembang, where a refinery was built. The prominent feature of the Sumatran petroleum is the large percentage of spirit suitable for distillation. This spirit has become a very important article of commerce, and its importation into Great Britain has been of the greatest service to the automobile industry, as the supplies of motor spirit would otherwise have been inadequate to meet the rapidly growing demand.

**Borneo.** The pioneers in petroleum development in Borneo were the Shell Transport and Trading Company, whose operations were transferred to the *Nederlandsche Handel Maatschappij*. The territory over which the company acquired exploitation rights is situated on the southern half of the east coast of Borneo, and has an area of 500 or 600 square miles. It is bounded on the north-east by the Kutei or Mahakkam River, and it extends towards the south to Balik Papan Bay, but it embraces also a strip of land on the south of the bay. Drilling operations were commenced in December, 1896, but were not actively carried on until a year or two later. The company has drilled a large number of wells, of which the maximum depth is about 1500 feet, and many of these have been flowing wells yielding abundantly. The crude oil at first obtained at shallow depth was an asphalt-base petroleum of high specific gravity, but subsequently a lighter oil of the same character was obtained at greater depth, and still later a paraffin-base oil of high commercial value was found. The company's refinery is situated on the northern shore of Balik Papan Bay. The asphalt-base petroleum of Borneo gives a large yield of excellent fuel oil, and from the paraffin-base petroleum all the usual commercial products, including paraffin wax, are obtained.

**Java.** The petroleum industry of Java owes its inception to the enterprise of the brothers Stoop, whose interest in the industry was taken by the Dordtsche Petroleum Maatschappij. In the year 1886 the industry has been rapidly progressive, and now occupies an important position. The chief producing territory is situated due south and south-west of the town of Surabaya, but there are also prolific deposits in the residency of Rembang. The depth of the wells range from 500 to 800 feet, and the drilling is chiefly done by the water-flush system. The average production of the wells is not large, but the yield is satisfactorily maintained. The crude oil has a sp.gr. of 0.825 to 0.916, and it yields a large proportion of solid hydrocarbons (paraffin) of unusually high melting-point.

#### *British India.*

**Burma.** At the end of the eighteenth century Major Symes described the petroleum wells 5 miles east of Yenangyaung, on the Irrawadi,

<sup>1</sup> The Bataafsche Petroleum Maatschappij, of the Hague, now own or control all the petroleum production in the Dutch East Indies.

as supplying 'the whole Empire and many parts of India with that useful product.' At that time the oil was obtained by the natives from shallow hand-dug wells, but since operations have been actively conducted in this and other districts by the Burmah Oil Company, Ltd., a British organisation which was the pioneer in the present petroleum industry of Burma. The principal yield is obtained from the Khodoung field, immediately adjoining the areas on which the native wells were dug; but oil is also found at Singu and at Yenangyat, respectively about 25 miles nearer to, and 25 miles further from, Rangoon. The Khodoung oil has a sp.gr. ranging from 0.731 to 0.904, and the Yenangyat oil ranging from 0.770 to 0.890. The wells are drilled by the American system. Formerly the crude oil was conveyed by bulk-barges on the Irrawadi to the refineries at Rangoon, but the Burmah Oil Company has recently completed a pipe-line 275 miles in length from the fields to the refineries. The company is under contract to supply the British Admiralty with oil fuel for the Navy, and has expended a large sum of money in making provision for this.

**Assam.** The Assam Oil Company, Ltd., has acquired the petroleum interests of the Assam Railways and Transport Company, Ltd., and the Assam Oil Company, Ltd., and is continuing the work carried on by those companies in the Digboi field with uniformly successful results. The company has a refinery where all the usual commercial products, including paraffin wax, are manufactured.

#### *Mexico.*

The Mexican Eagle Oil Company, Ltd., own large areas of proved petroliferous lands, and three fields are at present being exploited at Tanguijo, Tierra Amarilla, and Potrero del Llano, in Northern Vera Cruz. Fuel oil from these fields is now being transported by the Mexican Railway, the Gulf and Central Railway, and the crude oil is refined at the company's refinery at Tanguijo, which was recently acquired from the American Oil Company of S. Pearson and Son, Ltd., who for some years have systematically explored the Isthmus region, where they have several hundred thousand acres of petroliferous lands. Several other companies are also taking part in the development of the Mexican petroleum industry.

An illustration of the difficulties and disappointments met with in the exploitation of oil lands is furnished by the following particulars of a well drilled at Dos Bocas in 1908. This well had reached a depth of 1824 feet, when a petroliferous formation charged with oil under immense pressure was suddenly and unexpectedly encountered. Less than twenty minutes the ground round the well began to tremble and fissures appeared, some at a distance of as much as 250 feet from the well, from which oil and gas were discharged. One of these fissures extended under the boiler, and the gas was ignited. The well burned for 58 days,

during which time the oil consumed was estimated to have amounted to 3,000,000 barrels. The flame reached a height of nearly 1500 feet, and at the broadest part had a diameter of nearly 500 feet. So bright was the light emitted that a newspaper was read by it at a distance of 11 miles. In addition to oil and gas, the well discharged immense quantities of water, at times at the estimated rate of 1,500,000 barrels a day, and with the liquid about 2,000,000 tons of solid matter was ejected, a crater being thus formed which ultimately had an area of 117,600 square metres. The fire was eventually extinguished by pumping sand into the crater.

The petroleum industry in Mexico is rapidly increasing, and that country is now third in rank among the oil-producing countries of the world.

#### *Japan.*

The Japanese oil-fields extend from the western shore of Saghalin in the north, through the western part of the highlands of Hokkaido, and along the coast of the Sea of Japan, and the provinces of Mutsu, Ugo, and Shinano, reach to the coast of the Pacific Ocean in the province of Totomi in the south. There is also an oil-field in the northern part of the west coast of Formosa. The chief centre of the industry is in the province of Echigo, which produces about 99 p.c. of the total output of petroleum in Japan. The usual depth of the wells is from 600 to 1200 feet, and the American system of drilling is employed.

#### *Germany.*

Petroleum is found at Wietze, Steinförde, Oelheim, and elsewhere in the kingdom of Hanover; at Lobsann, Pechelbronn, Schwabweiler, and elsewhere in the kingdom of Prussia, in Lower Elsass, in Upper Elsass; and in the kingdom of Bavaria. The crude oil from the Steinförde district has a sp. gr. of 0.890 to 0.930. The sp.gr. of the Hagenau oil is 0.873, and that of the Tegernsee oil is 0.812.

#### *Peru.*

The petroliferous region of Peru extends about 250 miles in a northerly and southerly direction between the town of Tumbes, on the Gulf of Guayaquil, and Point Aguja, and about 150 miles east and west, from the Pacific coast to the slopes of the Andes. The northern fields, which are in the province of Tumbes, stretch from the Zarumilla River, which divides Peru from Ecuador, to the Mancora gully. The central fields comprise a part of the province of Paita, and extend from the Mancora gully to the south of the Silla de Paita and Toca point. The southern fields are situated in the province of Piura. The petroleum found in the hacienda La Mina Brea and Pariñas, which lies in the central portion of the petroliferous zone, was utilised by the Incas for centuries, and in the time of Pizarro it was collected in trenches and converted, by boiling it down, into a pitch of excellent quality. The petroleum was kept in porous earthen jars and transported therefrom in kegs and transported their fermented liquors. In 1867, Mr. Prentice, a Pennsylvanian petroleum producer, commenced drilling wells in the Zorritos

field, at the northern end of the belt, and subsequently disposed of the property to the Faustine G. Piaggio Petroleum Company. The crude oil has a sp. gr. of 0.810 to 0.840, and is rich in the more volatile hydrocarbons. In 1888 the hacienda La Mina Brea and Parifias was acquired by Dr. Tweddle, and the London and Pacific Petroleum Company was formed. The area of the property is 600 square miles. The crude oil has a sp. gr. of 0.834 to 0.848, and yields as much as 18 p.c. of benzine. The Lobitos Oilfields, Ltd., is a British company, formed in 1908 to acquire the properties of the Peruvian Petroleum Syndicate, Ltd. The company's Lobitos property comprises an area of about 25 square miles on which a large number of productive wells have been drilled. The company also has drilling rights on a further 4560 acres in the Punta Restin oilfield, about 13 miles north of Lobitos.

#### Canada.

Canadian petroleum has been obtained hitherto only in the province of Ontario, although it occurs in other parts of the dominion. The petroliferous region of Ontario has an area of about 100 miles by 50 miles, but the developed territory is mainly confined to a belt 16 miles by 2 miles, situated about 16 miles east of Sarnia and extending nearly parallel with the St. Clair River. The sinking of wells in the Enniskillen district has opened up a new petroleum industry equal in age to that of the United States. Although many of the Canadian wells have yielded largely at first, their output has in most instances quickly diminished, and the production is mainly obtained from a large number of wells yielding only a few gallons each daily. Natural gas is also found in Ontario, and is utilised as a source of light and heat. The largest area over which petroleum indications occur in Canada lies in the region of the Athabasca and Mackenzie rivers, in the north-west part of the dominion, where immense deposits occur of so-called 'tar sands,' first pointed out by Mr. J. A. Ross, estimated that the amount of bitumen contained in the sands amounts to 28.4 cubic miles, and that they contain 6.5 cubic miles, or 4,700,000,000 tons, of bitumen.

**New Brunswick.** The Maritime Oilfields Company, Ltd., are carrying out drilling operations under a concession, of an exceptionally favourable character, granted by royal charter in 1900, which gave the right to search for oil and gas over an area of 18,000 square miles and to select 10,000 square miles (more than one-third of the area of the province). The area selected is situated in the counties of Westmoreland, Albert, King's, Queen's, Sunbury, Kent, Northumberland, Gloucester, Restigouche, and a portion of York, and is traversed by several anticlineals, on one of which, in Westmoreland county, wells have been drilled successfully, a large yield of natural gas, in addition to oil, having been obtained. The crude petroleum is of excellent quality, with a paraffin base, and yields, in addition to 34 p.c. of kerosene, a fuel oil of high calorific value, containing only 0.14 p.c. of sulphur.

#### Italy.

The collection of the petroleum of Miano Medesano was the subject of a concession granted by the Ducal Chamber in 1400, and the celebrated petroleum of Modena, at one time largely used for medicinal purposes, for lighting and in the preparation of varnishes and paint was discovered in 1640 by Ariosto. The petroleum of Montechino was known prior to the eighteenth century, whilst the deposits of Ozzano and Rigo di Fornovo did not attract attention until early in the nineteenth century and those of Neviano de' Rossi, Salsomaggiore and Lesignano de' Bagni were found still later. Petroleum from the wells of Amiano, on the Taro, was used for lighting the cities of Genoa, Parma, and Borgo San Donnino as early as 1802. The districts in Italy in which petroleum is found in commercial quantities are (1) the zone of Emilia; (2) the valley of the Po in the province of Cuneo; and (3) the valley of the Liri, near San Giovanni Incarico, about midway between Rome and Naples. The zone of Emilia occupies the southern parts of the provinces of Piacenza, Parma, Modena, and Bologna. Some of the Italian crude petroleum has a specific gravity as low as 0.805, and is of amber colour, but unfortunately the quantities hitherto obtained have been small.

#### Other sources of supply.

In addition to the sources specified in the tabular statement of production, and some others incidentally mentioned in the preceding account, there are several potentially important petroleum-producing countries to which attention should be directed.

#### Persia.

The occurrence of petroleum in Persia has been mentioned by travellers from very early times, and its collection from the pits of Kirur Susiana (Kirab), 57 miles north-west of Shuster, was fully described by Herodotus. The petroleum is obtained in a general way from the Turco-Persian frontier, about 100 miles north of Bagdad and the Persian Gulf. In the course of surveys conducted a few years ago, specially favourable indications were found in two districts, on Zohab, in lat. 34° 18' N., long. 45° 55' E., and other near Shuster and Ahwaz, on the Karun River, at the head of the Persian Gulf. In 1903-4 two wells were drilled at Tehieh Sou near Kasr-i-Shirin, in the Zohab district, Mr. W. K. D'Arcy, under a unique concession granted by the Shah, giving petroleum rights over the whole Persian Empire, with the exception of certain provinces on the Caspian. One of these wells began flowing at a depth of 800 feet, and the other, at a greater depth from the crest of the anticline, reached a depth of 2100 feet. The crude petroleum had a specific gravity of 0.815, and was of exceptionally high quality. Subsequently the Burmah Oil Company, Ltd., became associated with Dr. D'Arcy in the conduct of the development, and drilled several highly productive wells in the second of two districts referred to. In 1909 the Anglo-Persian Oil Company, Ltd., was formed to take over the concession, and has actively continued



the work. The company is constructing a refinery and laying a pipe-line. It may here be mentioned that the Persian petroleum deposits extend into Turkey, and that very promising indications are met with in Mesopotamia.

### *Egypt.*

The oil deposits of the Red Sea have been known from time immemorial, but attention was specially directed to them during the latter part of the last century by the successful results of the exploratory work carried out by de Bay at Jebel-Zeit, about 160 miles from Suez, and Jemsah, 13 miles south of Jebel-Zeit. In 1905 the Egyptian Petroleum Company, Ltd., acquired a concession over a large area at Jemsah. In 1907 the Egyptian Oil Trust, Ltd., took over the concession, and drilled a number of highly productive wells. On a portion of the area the work has been continued by the Red Sea Oilfields, Ltd., which was formed in 1910. The Anglo-Egyptian Oilfields, Ltd., the management of which is vested in the Anglo-Saxon Petroleum Company, Ltd., has recently acquired the licenses and assets of the Egyptian Oil Trust, Ltd., with a view to the active development of the field, and shipments of the crude oil have already been made. Drilling operations are also being conducted by the Sinai Petroleum Syndicate, Ltd., on the Sinai Peninsula.

### *Trinidad.*

The 'Pitch Lake' of Trinidad, which is the most important, if not the largest, deposit of solid or semi-solid bitumen, was visited in 1595 by Sir Walter Raleigh, who reported that he saw there 'that abundance of stone pitch that all the ships in the world might be laden from thence.' The area of the deposit is about 100 acres, and on the basis of an average depth of 20 feet, the quantity of the material obtainable has been estimated at over 3,000,000 tons. Gesner states, in his *Treatise on Coal, Petroleum, &c.* (New York, 1861), that it was from Trinidad asphalt that he first prepared kerosene.

Petroleum apparently occurs over a great part of the southern half of the island. The first important concession of oil-bearing territory was granted some years ago, on the initiative of Mr. Randolph Rust. It embraces an area of more than 50 square miles at Guayaguayare in the south-eastern corner of the island. Although the early drilling operations were attended with success, the concession was made in the work of the Trinidad Petroleum Properties of Trinidad, Ltd. Among a large number of other companies recently formed to participate in the exploration and exploitation of the oil lands of Trinidad, one of the most important is Trinidad Oilfields, Ltd., which acquired the rights over areas in the Guapo and La Brea districts on which successful results had already been obtained by the Trinidad Petroleum Company, Ltd. It is, however, in the neighbourhood of the Pitch Lake that the greatest progress has been made. Here, through the enterprise of the American concessionaires of the lake and their associates, a number of prolific wells have been drilled, a refinery has been built, and the first shipment of the oil was made in the spring of 1911. There are grounds

for hope that Trinidad may become a source of oil fuel for the West Indies.

### *Barbados.*

The crude petroleum of Barbados, under the name of 'Barbados tar,' was formerly an article of commerce, and occupied an important place as a medicinal agent. It was obtained from a group of hand-dug shafts known as the Lloyd wells, in the Scotland district of the island. Drilling has been conducted in this district by the West Indian Oil Syndicate, Ltd., and subsequently by the West Indian Petroleum Company, Ltd., but only small quantities of oil have been met with.

### *Venezuela.*

The petroleum deposits of Venezuela resemble those of Trinidad, and will probably become of great commercial importance. There are many highly promising petroliferous areas of great extent, and in the State of Bermudez there is a deposit of asphalt far larger than the Pitch Lake of Trinidad.

### *Colombia.*

Remarkable indications of the presence of petroleum are reported to occur in Colombia. As many as 40 petroleum springs have been found at a distance of 1 to 3 miles from the Gulf of Uraba, near the Arboletes, one of which is said to yield enough oil to fill a six-inch pipe. Other springs occur on the plain of Medina, about 9 miles from the River Uquia, a tributary of the Meta.

### *Ecuador.*

The existence of petroleum in the Santa Elena district, about 64 miles west by south of the port of Guayaquil, has been known for more than two centuries, and the oil has from very early times been collected in a primitive fashion for local use.

### *Argentina.*

On the eastern slopes of the Sierras of the Andes, and elsewhere, there are promising indications of the occurrence of petroleum; but although in some localities oil has been found in quantity, drilling operations have not been generally successful.

### *Newfoundland.*

The existence of petroleum on the west coast of Newfoundland has been known for about a century, for it was in 1812 that Mr. Parsons, after whom Parsons' Pond is named, used the crude oil of this district as a cure for rheumatism. Drilling operations are now being conducted at Parsons' Pond.

### *Alaska.*

Several wells have been drilled in the neighbourhood of Katalla and excellent results obtained, in respect alike of the abundance of yield and of the quality of the oil. The producing territory has been acquired by the Amalgamated Development Company, an organisation in which Canadian capitalists are largely interested.

### *New Zealand.*

The petroleum indications occur (1) in the neighbourhood of the west coast of the island at New Plymouth and on the adjacent



Sugar Loaves Islands; (2) on the east coast along a belt of country extending from Horocra Point, near the East Cape, to the Okahuatin Block, 30 miles west of Gisborne (Poverty Bay); and (3) at Kotuku, near Lake Brunner, South Island. Wells drilled at New Plymouth have yielded petroleum of excellent quality, with a sp.gr. of 0.840, and containing a large proportion of solid hydrocarbons. The exploratory drilling carried out many years previously in the Poverty Bay district was not attended with success, but as the result of further recent study of the geological conditions, it is hoped that both here and in the Taranaki district a large output may eventually be obtained.

#### THE TESTING OF CRUDE PETROLEUM AND OF PETROLEUM PRODUCTS.

##### 1. Crude petroleum.

The examination of crude petroleum which the chemist is called upon to conduct in the laboratory for commercial purposes usually includes the estimation of water and sediment, the ascertaining of the specific gravity, flashing-point, and viscosity, and the character of the products.

The test recommended by Engler gives most useful information in regard to the commercial value of a sample of crude petroleum. It consists in carefully distilling the oil in a Wurtz flask, and noting the percentages of distillate obtained below 150° F. and either 300° F. if the hydrocarbons present are mainly those of the methane series, or 285° F. if they are principally naphthenes, the first fraction consisting of benzene and the second of kerosene.

The natural lubricating oils (crude petroleum) of Pennsylvania, Ohio, West Virginia, and Kentucky have been classified by the West Virginia Transportation Company according to specific gravity, and subjected to the following test:—

In receiving and making delivery of oils the water and sediment are determined by mixing an average sample with an equal quantity of benzene, and subjecting the mixture to 120° F. in a graduated glass vessel for not less than six hours, after which the mixture cools and settles not less than two hours for light grades, three hours for A grade, four hours for B grade, six hours for C grade, eight hours for D grade, and eighteen hours for heavier grades. The grades are as follows:—

A. 37.1° Baumé (about 0.838 sp.gr.) and lighter.

B. 33° to 37° B. (0.859 to 0.838 sp.gr.).

C. 31.6° to 32.9° B. (0.870 to 0.859 sp.gr.).

D. 30.6° to 31.5° B. (0.873 to 0.872 sp.gr.).

E. 29.6° to 30.5° B. (0.877 to 0.873 sp.gr.).

F. 28.6° to 29.5° B. (0.883 to 0.877 sp.gr.).

G. 28.5° B. (0.883 sp.gr.) and heavier.

Ordinary crude petroleum, from which kerosene and the other usual commercial products are manufactured, is in the United States required to conform to the following rule of the New York Produce Exchange, except in regard

<sup>1</sup> In the case of the more viscous descriptions of petroleum, the writer finds that further dilution is desirable. The benzene used should be previously saturated with water.

to specific gravity, as to which the restriction has been relaxed, in consequence of the fact that much of the crude petroleum now obtained has a specific gravity Baumé below 43°:—

'Crude petroleum shall be understood to be pure natural oil, neither steamed nor treated, free from water, sediment, or any other adulteration, of the gravity of 43° to 48° B. (0.809 to 0.786 sp.gr.).'

In order to determine whether the petroleum is a 'pure natural oil' a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the specific gravity of the several distillates is determined. The following results obtained in the examination of two typical samples indicate the form of the certificate handed to the buyer:—

##### Oil from Parker District. Gravity 46° Baumé.

1st Product . 72° B.	6th Product . 46° B.
2nd " . 62° B.	7th " . 42° B.
3rd " . 57° B.	8th " . 41° B.
4th " . 53° B.	9th " . 42° B.
5th " . 49° B.	

##### Oil from Bradford District. Gravity 43° Baumé.

1st Product . 71° B.	6th Product . 41° B.
2nd " . 60° B.	7th " . 40° B.
3rd " . 54° B.	8th " . 41° B.
4th " . 49° B.	9th " . 42° B.
5th " . 45° B.	

The regular gradation in the specific gravities of the fractions examined in the above certificates is taken to indicate that the oil is a natural product.

The examination of a sample of crude petroleum with the object of determining the percentage of commercial oil is not always an easy operation, especially when the quantity available is small. The writer is accustomed to conduct the fractional distillation in a glass retort embedded in sand, and to compare the results obtained with those furnished by samples of crude petroleum the yield of products from which on the commercial scale is known, but even in these circumstances some experience is needed in certain cases. The difficulties encountered arise from the circumstances that in practice in the United States some of the intermediates are 'cracked,' and thus pass over to a larger extent than usually occurs when the distillation is conducted in a small retort in the laboratory, and that, on the other hand, the heavy hydrocarbons composing the lubricating oil are less 'cracked' when properly distilled with the aid of steam on the large scale than when distilled on the small scale. The determination of the percentage of solid hydrocarbons is also attended with considerable difficulties when the quantity of material operated upon is small. In every case the aim should be to reproduce as far as possible the conditions of practical working.

##### 2. Petroleum spirit.

In the testing of petroleum spirit, including petrol, gasoline, benzene, &c., it is usual to determine the specific gravity and range of boiling-points, and the writer finds it desirable to make a fractional distillation of the sample in order to ascertain the percentage boiling below a series of temperatures increasing

by regular intervals. 100 c.c. should be distilled from a Wurtz flask which is supported on a sand dish and has the following dimensions:—

Bulb  $2\frac{1}{2}$  ins. in diameter; neck  $\frac{3}{4}$  ins. in diameter,  $5\frac{1}{2}$  ins. long; exit tube  $2\frac{1}{2}$  ins. above shoulder. The tube of the Liebig condenser employed is 24 ins. long. The thermometer having been adjusted with its bulb at first just immersed in the liquid, is gradually raised, as soon as ebullition becomes active, so that its bulb is slightly below the rising level of the vapour (which can be seen with a strong illumination). The temperature at which the first drop falls from the end of the exit tube of the flask is taken as the initial boiling-point of the sample. The percentages collected in a 100 c.c. measure glass at different thermometer-readings are recorded, together with the final boiling-point, or temperature at which the flask becomes dry. Deodorised American petroleum spirit should have no disagreeable odour either in bulk or when evaporated on the hand. A small quantity evaporated in a basin over the water-bath should leave no oily residue. When petroleum spirit is used as a turpentine-substitute in paints it is important that it should contain no sulphur compounds. For the detection of these the sample may be boiled for a few minutes with alcohol and a few drops of ammonia, and nitrate of silver solution then added, when there should be no brown colouration.

The presence of sulphuric acid may be detected by agitating the spirit with warm water, separating the water (which should exhibit no acid reaction), and adding to it a few drops of barium chloride solution.

### 3. Kerosene.

For ordinary commercial purposes the only characteristics which are noted in the examination of kerosene are the colour, the odour, the specific gravity, and the flashing point or fire-test. In certain cases, however, special tests are applied with the object of ascertaining whether the oil is of satisfactory burning quality, is of natural composition, has been properly treated with acid, has been sufficiently washed, and is free from sulphuric acid, carbonates, and sulphur in other forms.

(a) *Colour.*—It was the practice to estimate the colour of a sample by comparing it with that of a standard sample, the two oils being placed in bottles of the same size. Such a method did not, however, admit of an accurate comparison being made, and in the year 1870 the writer adopted the plan of placing the samples in long glass cylinders which were held in a frame in such manner that the images of the glass bottoms of the cylinders could be viewed side by side in a mirror. This arrangement was found to present marked advantages.

In the case of a fluorescent liquid like petroleum, but the system was open to the objection that the standard samples were very liable to become altered in colour, and required to be frequently verified and corrected by experts. Moreover, the adoption by the Petroleum Association of London of precise conditions of contract necessitated the provision of a more accurate and unerring test of colour. Accordingly, the Committee of the Petroleum Association decided, under the advice of the writer, to employ an instrument devised by Mr. R. P. Wilson for

use with stained glass standards. This apparatus (Fig 2), which has admirably fulfilled the object in view, consists of two similar tubes, closed at each end by a screw cap carrying a disc of stout glass. These tubes are placed on a stand at a convenient angle above a small mirror, by means of which light is reflected upwards through them. At the upper ends of the tubes is a box containing pairs of prisms so arranged that light from the mirror

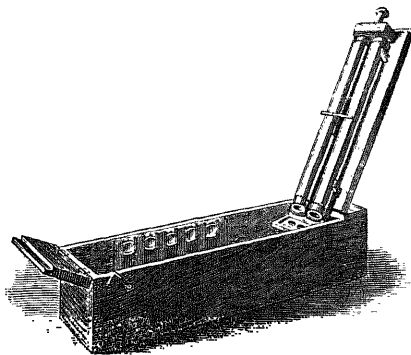


FIG. 2.

is twice reflected, and is thus brought into an eye-piece surmounting the box. One of the tubes is completely filled with the sample of oil to be tested, the length of the column of liquid being sixteen inches, and beneath the other tube, which remains empty, a disc of stained glass is placed. On applying the eye to the eye-piece the circular field is seen to be divided through the centre by a sharp line formed by the junction of the prisms, the two halves being tinted to an extent corresponding with the colour of the oil and the colour of the glass respectively. The glass standards representing the various grades of colour recognised in the trade are prepared by the Messrs. Schmidt and Haensch. They are five in number:

1. Water white.
2. Superfine white.
3. Prime white.
4. Standard white.
5. Good merchantable.

The Wilson chromometer admits of an accurate comparison being made, but where the colour of the sample is very pale, and those of two standards, there is an absence of precision in the statement of the result of the test. This is not attended with any practical inconvenience where the instrument is simply used for ordinary routine work, but the writer has frequently found it necessary to record the precise colour of a sample, or to state by how much that colour falls short of a stipulated grade. To meet this want a modification of the chromometer already described was designed by Stammer. In this apparatus there is a provision for shortening the length of the column of oil, so that, starting with a standard of somewhat paler tint than the oil, the colour of the oil may be registered in terms of the standard. Messrs. Schmidt and Haensch, the well-known philosophical instrument makers of Berlin, have devoted a good deal of attention to the improvement of Stammer's original instrument, and have devised a

colorimeter which the writer has used, and of which he has formed a favourable opinion. In the construction of this apparatus (Fig. 3) Messrs. Schmidt and Haensch have desired to provide for the use of only one glass standard,

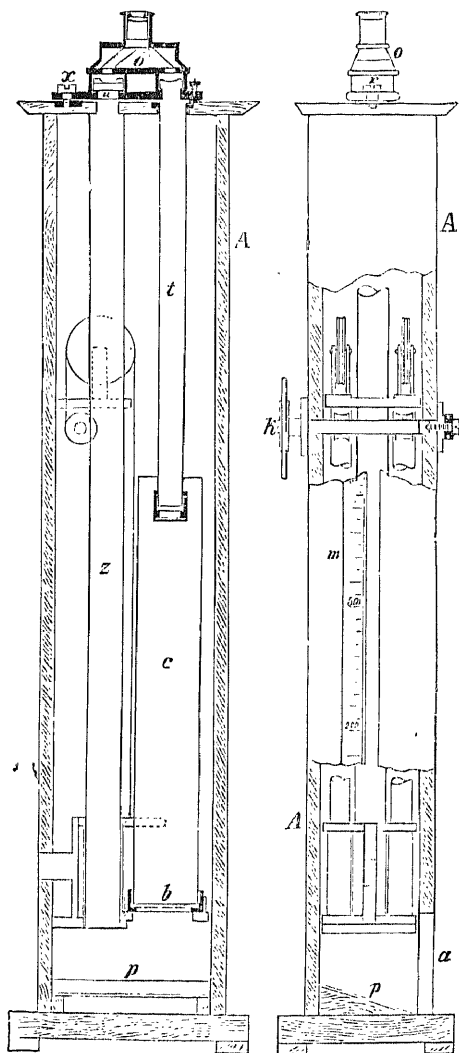


FIG. 3.

A. Case. a. Opening for passage of light to reflector. b. c. Cylinder, with glass bottom, for oil under examination. k. Hand-wheel for raising or lowering cylinder b. c. m. Graduated scale showing length of column of oil through which light is passing. o. Optical arrangement for projecting light. p. Reflector to project light into the oil. z. Prism to turn the light into the oil. v. Valve by which the oil can be turned to insert or remove the oil. The oil can be turned to insert or remove the oil.

so that all recorded determinations of colour may be strictly comparable. This would be a distinct advantage, since the relation between the various standards enumerated is a purely arbitrary one; but unfortunately the range of colour is neces-

sarily so wide that if a standard suitable for water-white oil is employed, the column needs to be so much decreased in length for oils of dark colour that the sensitiveness of the instrument is seriously impaired. To overcome this defect, Mr. Robert Redwood has made several important alterations in the instrument, which, while largely increasing its sensitiveness, admit of the colour of any sample of kerosene being precisely recorded on a scale ranging from water white (1) to good merchantable (5), the space between any two of the colours being divided into ten equal parts, so that the colour of a sample midway between water white and superfine white would be expressed as 1.5. This instrument has been in use in the writer's laboratory for many years, and has given very satisfactory results.

(b) *Odour*.—The determination of odour requires considerable experience, as it is necessarily a matter of judgment, and due consideration has to be given to the origin and grade of the oil. It is usual to certify that the odour is good merchantable, or not good merchantable, as the case may be.

(c) *Specific gravity*.—This is ordinarily determined by the use of a hydrometer, but the Westphal or the Sartorius specific gravity balance will often be found a preferable instrument. In the case of oil imported in bulk, where the weight of the oil is calculated from the volume at a given temperature, the specific gravity should be accurately determined by the use of the specific gravity bottle.

(d) *Flashing-point and fire-test*.—This is, at any rate from one point of view, by far the most important test to which kerosene is subjected, since the petroleum trade is in most parts of the world conducted under legal restrictions in regard to the temperature at which the oil either commences to evolve inflammable vapour or takes fire and continues to burn. The manufacturer of kerosene has on the one hand to avoid introducing into or leaving in the oil such of the more volatile hydrocarbons as would cause it to flash at a temperature below the limit of the ordinary construction, and on the other hand to arrest the collection of the kerosene distillate before the process of distillation has resulted in the addition to the product of the denser hydrocarbons in such quantity as to impair the burning quality. The limitation of the specific gravity was found to be an effectual means of preventing the introduction into the oil of an undue proportion of the heavier hydrocarbons, but afforded no check upon the inflammability of the oil; accordingly, in the early days of the petroleum industry, it was customary in the United States to test the oil by pouring it upon warm water and applying a lighted taper to the surface, or by warming the oil in a cup placed in hot water, and applying a flame, the temperature at which the oil gave off ignitable vapour being termed the 'flashing-point,' and that at which it took fire the 'fire-test.' When, however, it became recognised that legal restrictions in regard to the inflammability of kerosene were necessary in the interests of public safety, special forms of testing instruments were devised. The earliest of these testing instruments, known as

Tagliabue's open-cup tester (Fig. 4), was constructed by an instrument-maker of that name in New York. It consists simply of a glass cup

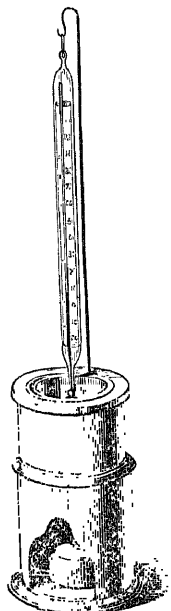


FIG. 4.

to hold the oil, placed in a small copper water-bath, heated by a spirit lamp. A thermometer is suspended in the oil, and the temperature is noted at which, on passing a lighted splinter of wood across the surface of the oil, there is either a flash of ignited vapour, or on a further increase of temperature the oil ignites and continues to burn. The English Petroleum Act, passed on July 29, 1862, provided that 'Petroleum for the purposes of this Act shall include any product thereof that gives off an inflammable vapour at less than 100° of Fahrenheit's thermometer.' The method of testing was, however, not defined, and the Act was practically inoperative. Accordingly, on July 13, 1868, an amending Act was passed, which prescribed the form of apparatus and method of testing to be adopted, and defined 'petroleum' for the purposes of the two Acts as including 'all such rock oil, Rangoon oil, Burmah oil, any product of them, and any oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any product of them, as gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer.' The prescribed apparatus for testing consists of a slightly conical oil cup of thin sheet-iron, provided with a flat rim, and a raised edge  $\frac{1}{4}$  in. high. Across the cup and fixed to or resting on the edge is a wire, which is thus  $\frac{1}{4}$  in. above the flat rim. The oil-cup is supported by the rim in a tin water-bath. The outer vessel having been filled with 'cold or nearly cold water,' as much of the oil to be tested is poured into the cup as will fill it without flowing over the flat rim, and a thermometer with a round bulb, and so graduated that every 10°F. occupies not less than  $\frac{1}{2}$  in. on the scale, is then suspended in the oil so that the bulb is immersed about 1  $\frac{1}{2}$  in. beneath the surface. A screen of paste-board or wood of specified dimensions having been placed round the apparatus, a 'small' flame is applied to the bottom of the water-bath, and when the temperature of the oil has reached 90°F., a 'very small' flame is passed across the surface of the oil on a level with the wire, this application of the test-flame being repeated for every rise of 'two or three' degrees in temperature, until a 'pale-blue flicker or flash' is produced. The temperature at which this occurs having been noted, the experiment is repeated with a fresh sample of the oil, the source of heat when the temperature approaches that noted in the first experiment, and applying the test-flame at every rise of two degrees.

The greater part of the earlier petroleum legislation in the United States was based upon fire-test and not upon flashing-point, but in several of the States the petroleum laws now prescribe a test of flashing-point. In 1879 the New York Produce Exchange adopted the Saybolt Electric Tester (Fig. 5), which is an open-cup instrument wherein the ignition is effected by means of an electric spark from a small induction coil, the spark being caused to pass when required between platinum points at a fixed distance above the surface of the oil. The official directions for the use of the apparatus are as follows:—

'Fill the metal bath with water, leaving room for displacement by the glass cup. Heat the water until the bath thermometer indicates 100°F., at which point remove the lamp. Fill the glass cup with oil to top line, indicated by the rim surrounding cup, which is one-eighth of an inch below top edge of the cup. See that there is no oil on the outside of the cup, nor upon the upper level edge, using paper to clean cup in preference to cotton or woollen material. See that the surface of the oil is free from air

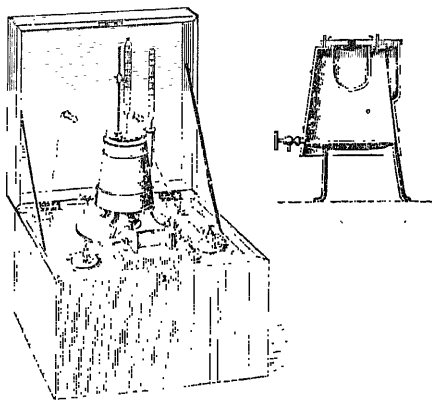


FIG. 5.

bubbles before first flash is produced. Lift the cup steadily with left hand and place in the bath. Suspend the thermometer with the bulb of same immersed just from view under the surface of oil. Adjust the flashing bar and immerse the battery zincs in fluid. Try for first flash every degree until the same is obtained. Attain flash by producing spark with one stroke of the key. The stroke on the key should be such as in telegraphy is used to produce what is called a dot, that is a short quick stroke. The first flash produced from 110° test oil is generally obtained when the temperature of the oil has arrived at 90°. The temperature of the bath at 100° (as per note above) will carry the oil to about 90°, or, in other words, to about the first flash-point, without the aid of a lamp. When the thermometer in the oil indicates 90°, introduce lamp under the bath, and do not remove until the operation is finished. The temperature of oil when placed in bath should not be lower than 55° nor higher than 70°F. The flashing bar must be free from oil before adjusting for test. Draughts of air must be excluded from the apartment wherein tests are made.

Oil of 110° and upwards shall (after first flash) be flashed at 95, 100, 104, 108, 110, 112, 115. Oil of 120° and upwards, after first flash, 100, 105, 110, 115, 118, 120, 122, 125. Oil of 130° and upwards, every five degrees after first flash, until burning-point.'

Prior to the introduction of the Saybolt Tester, Arnaboldi constructed an open-cup tester similar to Tagliabue's, but of greater capacity, and provided with a mechanical arrangement for passing the test-flame over the oil.

The directions for applying the test given in the English Petroleum Act of 1868 were found to be insufficiently precise, and much difference of opinion existed as to the interpretation of the words 'small flame' and 'very small flame,' with the result that dealers were proceeded against, and in some cases convicted of selling kerosene declared by the local authorities to have a flashing-point below the legal limit of 100°F., but which had been tested by independent experts with satisfactory results. Moreover, the open-cup system of testing was found by

experience to be incapable of furnishing trustworthy results in the hands of unskilled persons.

Accordingly, Mr. Keates, in his capacity of consulting chemist of the Metropolitan Board of Works, suggested the substitution of a closed cup (Fig. 6) for the open one, and in 1871 a Bill to legalise this alteration, as well as to amend the law in several other respects, was introduced into Parliament. In consequence, however, of the test standard or limit having been fixed by Mr. Keates at a point (85°) which it was contended was considerably higher than the equivalent of the existing standard, the

Bill was opposed by the petroleum trade, and the proposal to change the form of apparatus was withdrawn; the Bill, which passed through the final stage on August 11 in that year, repealing the two previous Acts, but again prescribing the use of the open test specified in the Act of 1868. In the following year the subject of petroleum testing was inquired into by a Select Committee of the House of Lords, and a great deal of conflicting evidence was taken, but no satisfactory conclusion was arrived at. Therefore, in July 1875, with the concurrence and approval of the Metropolitan Board of Works and of the Petroleum Association, Sir Frederick Abel was requested by the Government to undertake an investigation with the object of placing the subject of petroleum testing upon a satisfactory basis. The formulated questions submitted to Sir Frederick Abel were the following:

1. Whether the method of testing petroleum

as prescribed in Schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is such as uniformly to ensure reliable and satisfactory results.

2. If not, what alterations in the method of testing petroleum should be adopted to secure such results, due regard being had to the fact that the testing must, in many instances, be carried out by persons who have had comparatively little experience in conducting delicate experiments.

3. Assuming it to be, in your opinion, desirable to obtain a "flashing-test" for petroleum, whether the present "flashing-point" of 100°F. (or its equivalent under any modified method of testing which you may propose) is, in your judgment, calculated to afford adequate protection to the public, without unduly interfering with or restricting the trade; if not, what alteration in this respect should be made.

After a prolonged and exhaustive experimental inquiry, in which Dr. Kellner rendered valuable assistance, Sir Frederick Abel presented to the Secretary of State an elaborate report, dated August 12, 1876, wherein the questions enumerated were thus answered:

(1) The method of testing petroleum as prescribed in schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is not 'of a nature uniformly to ensure reliable and satisfactory results.'

(2) A method of testing petroleum has been elaborated for adoption in place of that prescribed by the Petroleum Act, 1871, due regard having been had to the fact 'that the testing must in many instances be carried out by persons who have had comparatively little experience in conducting delicate experiments.' This method, in its general nature the oil is free from the defects inherent in the latter, and is so arranged that it can be carried out, with the certainty of furnishing uniform and precise results, by persons possessing no special knowledge or skill in manipulation. With ordinary attention in the first instance to simple instructions, different operators cannot fail to obtain concordant results with it, and it is so nearly automatic in its nature that it is not, like the present method of testing, susceptible of manipulation so as to furnish different results at the will of the operator.

(3) There are not, in my judgment, any well-established grounds for considering that the present flashing-point of 100°F. is not 'calculated to afford adequate protection to the public.'

(4) With the new test, a minimum flashing-point should therefore be adopted, which is equivalent, or as nearly as possible so, to the flashing-point of 100°F., as furnished by the present test.

It will be obvious that the determination of the equivalent test standard was not an easy part of Sir Frederick Abel's task, since the Abel tester furnishes no exception to the rule that the flashing-point of a given example of petroleum is far lower in a closed than in an open vessel, and it was therefore necessary to deal with the conflicting views already referred to as to the proper mode of conducting the test with the open-cup instrument in order to determine the equivalent standard. The writer assisted Sir Frederick Abel in the conduct of this portion

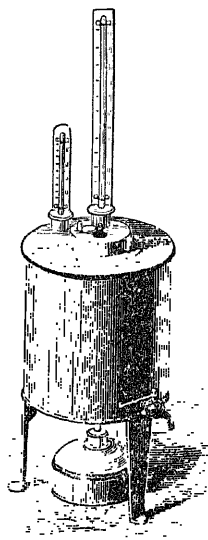


FIG. 6.

of the inquiry, but before the test standard was even provisionally fixed, Mr. T. W. Keates, as representing the Metropolitan Board of Works, and Mr. John Calderwood, on behalf of the Scottish Mineral Oil Association, were also consulted. Eventually, as the result of the joint experiments, it was decided that the difference between the flashing-points obtained with the open-cup instrument and the Abel tester ranged from  $25^{\circ}$  to  $29^{\circ}$ F. Adopting the mean difference of  $27^{\circ}$ , the new standard was accordingly fixed at  $73^{\circ}$ F.

After the presentation of the report, the

writer proceeded to apply the two tests to 1,000 representative samples of kerosene, with the result that the figures provisionally adopted were confirmed.

The ultimate outcome of Sir Frederick Abel's painstaking investigation was the legalisation by Parliament, on August 11, 1879, of what is now so well known as the Abel Test. The instrument and its use are thus described in the Petroleum Act:—

FIRST SCHEDULE.—Mode of testing petroleum so as to ascertain the temperature at which it will give off inflammable vapour.

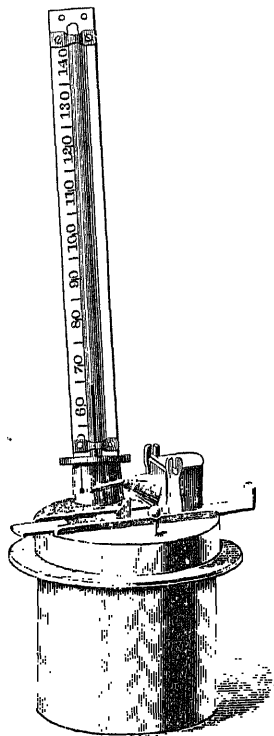


FIG. 7.

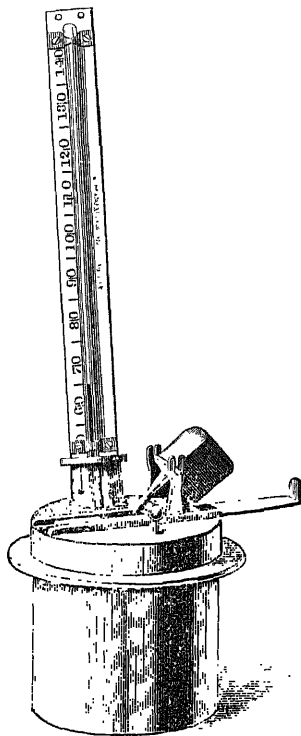


FIG. 8.

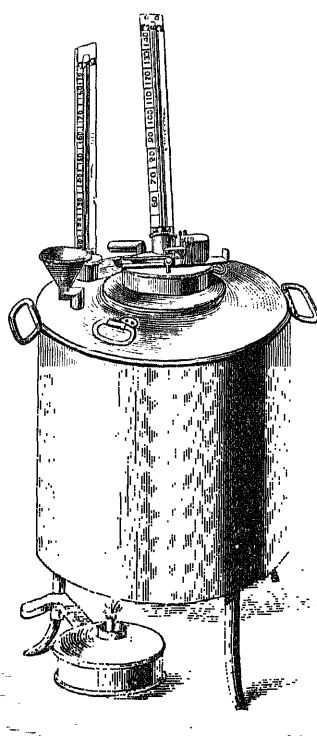


FIG. 9.

*Specification of the test apparatus*  
(Figs. 7, 8 and 9).

The following is a description of the details of the apparatus:—

The oil cup (Fig. 7) consists of a cylindrical vessel 2" diameter,  $2\frac{3}{16}$ " height in round, with outward projecting rim  $\frac{5}{16}$ " wide,  $\frac{3}{16}$ " from the top, and  $1\frac{3}{8}$ " from the bottom of the cup. It is made of gun-metal or brass (17 B.W.G.) tinned inside. A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is  $1\frac{1}{2}$ ". The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of

trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer, when inserted to its full depth, shall be  $1\frac{1}{2}$ " below the centre of the lid.

The cover is provided with three square holes—one in the centre,  $\frac{3}{16}$ " by  $\frac{1}{16}$ ", and two smaller ones,  $\frac{3}{16}$ " by  $\frac{3}{16}$ ", close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface

of the lid (Fig. 8). Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test-flame to be used.

The bath or heating vessel (Fig. 9) consists of two flat-bottomed copper cylinders (24 B.W.G.)—an inner one of 3" diameter and 2½" height, and an outer one of 5½" diameter and 5½" height; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to inclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about ¾"; that is, its diameter is about 5" greater than the body of the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil lamp is one-half of an inch. A split socket similar to that on the cover of the oil cup, but set at a right angle, allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is 8¾". One of the three legs of the stand serves as a support for the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is 1".

Two thermometers are provided with the apparatus—the one for ascertaining the temperature of the bath, the other for determining the flashing-point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about 90° to 190° Fahrenheit. The scale (in degrees of Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about 3½", measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about 55°F. to 150°F.; it measures from end of ivory back to bulb 2½".

NOTE.—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade.

#### *Directions for applying the flashing-test.*

1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

2. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130°F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

When a test has been completed, this water-bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0.15 of an inch diameter, and this size of flame, which is represented by the radiating lines on the cover of the oil cup, is maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil-lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° the samples to be tested should be cooled down (to about 60°) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5. The test-lamp is then placed in position upon the lid of the cup, the lead line or pendulum,<sup>1</sup> which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to

<sup>1</sup> The pendulum is 24 inches in length from the point of suspension to the centre of gravity of the weight. The writer has found it convenient to employ a synchronised metronome.

be commenced, the test flame being applied once for every rise of one degree in the following manner:—

The slide is slowly drawn open while the pendulum performs three oscillations and is closed during the fourth oscillation.

NOTE.—If it is desired to employ the test apparatus to determine the flash-point of oils of very low volatility, the work of proceeding is to be modified as follows:—

The air-chamber which surrounds the cup is filled with cold water to a depth of  $1\frac{1}{2}$  inches,

and the heating-vessel or water-bath is filled usual, but also with cold water. The lamp then placed under the apparatus, and kept the during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120° instead of with cold water.<sup>1</sup>

In order to deal with the difficulty arising from the sluggish flow of the convection current and the consequent low reading of the thermometer, when viscous samples are tested, and, in addition, to make provision for the testing of

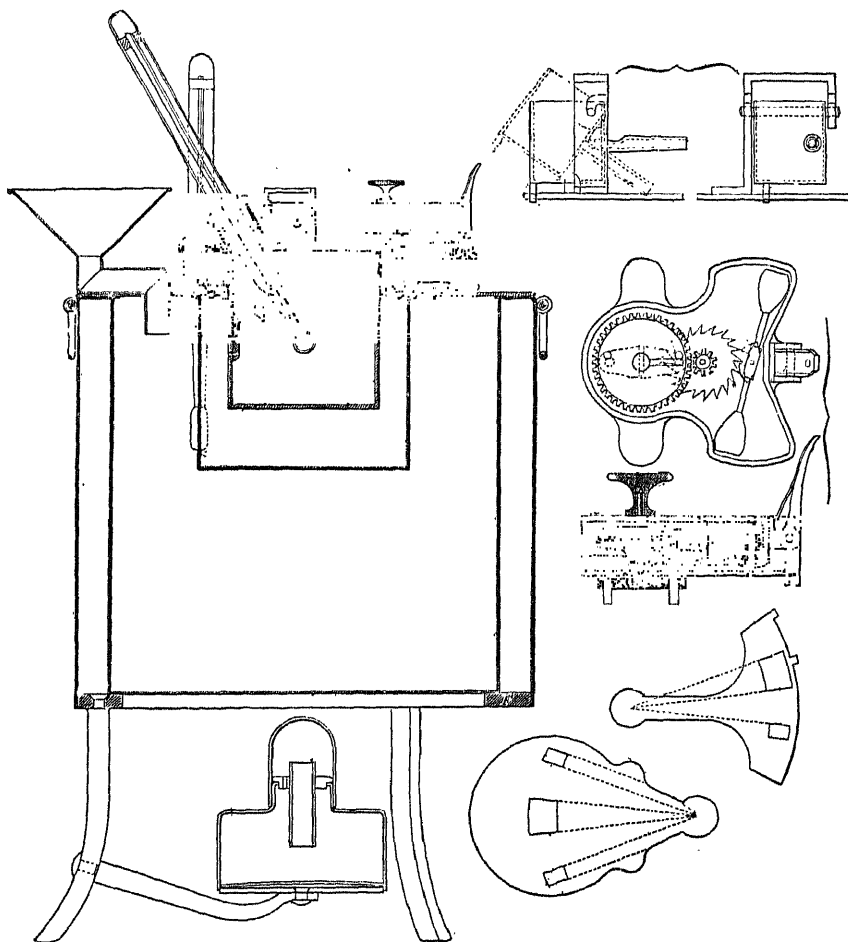


FIG. 10.

solid petroleum mixtures, an Order in Council (Statutory Rules and Orders, 1907, No. 483) was issued on May 7, 1907, the Schedule of which is as follows:—

SCHEDULE.—DIRECTIONS FOR TESTING PETROLEUM MIXTURES.

1. *Liquid Mixtures.* Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the

manner set forth in Schedule One to the Petroleum Act, 1879.

2. *Viscous and Sedimentary Mixtures.* Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner

<sup>1</sup> A preferable method is to keep the temperature of the water-bath at 130°F. and place water to a depth of a quarter of an inch in the air-space.



set forth in Schedule One to the Petroleum Act, 1879.

In carrying out such separation, care must be taken to minimise the evaporation of the petroleum. The separation of the sediment must not be effected by distillation.

Where the petroleum mixture is such that sediment cannot be separated by the aforementioned means, or where it is of a viscous nature, as in the case of indiarubber solution, quick-drying paints, &c., such mixture shall be tested in the apparatus modified as shown in the accompanying diagram. The apparatus differs from that set forth in Schedule One to the Petroleum Act, 1879, in the addition of a stirrer to be revolved throughout the sample under test.

The stirrer, for viscous petroleum mixtures, shall be constantly revolved at a slow speed with the fingers, except when applying the test flame, the direction of revolution being that of the hand of a clock.

With the exception of the use of the stirrer, the manner of carrying out the test shall be that set forth in Schedule One to the Petroleum Act, 1879.

The stirrer may be removed by grasping the spindle just above the blades with the finger and thumb, and pulling it out of its upper sheath. The opening in the sheath through which the stirrer passes, may then be closed by a plug provided for the purpose.

When this has been done, the apparatus shall be deemed to comply with the specification set forth in Schedule One of the Petroleum Act, 1879, and may be used for testing ordinary petroleum or solid petroleum mixtures.

A model of the above-mentioned apparatus will be deposited with the Board of Trade, and the provisions of section 3 of the Petroleum Act, 1879, in regard to verification and stamping shall apply also to such apparatus as though it were the apparatus prescribed by the said Act.

For the purpose of carrying out such verification the stirrer shall be removed and the opening in the sheath closed by the plug. The apparatus shall then be tested with ordinary petroleum. The stirrer shall be verified by comparison of measurements.

**3. Solid petroleum mixtures.** Where the petroleum mixture is solid, as in the case of naphtha soaps, &c., the apparatus to be used for the test shall be that prescribed in Schedule One of the Petroleum Act, 1879.

The method of carrying out the test of such solid mixture shall be as follows:—

The solid mixture must be cut into cylinders  $1\frac{1}{2}$  inches long and  $\frac{1}{4}$  inch in diameter by means of a cork borer or other cylindrical cutter having the correct internal diameter. These cylinders are to be placed in the petroleum cup of the testing apparatus in a vertical position in such number as will completely fill the cup. The cylinders must be in contact with one another, but must not be so tightly packed as to be deformed in shape.

Five or six of the cylinders in the centre of the cup must be shortened to  $\frac{1}{2}$  inch to allow space for the thermometer bulb.

The air bath of the testing apparatus must be filled to a depth of  $1\frac{1}{2}$  inches with water.

The water bath must then be raised to and maintained at a temperature of about 75°F.

The cup must then be placed in the air bath, and the temperature of the sample must be allowed to rise until the thermometer in the oil cup shows 72°F., when the test flame must be applied.

If no flash is obtained, this temperature must be maintained constant in the oil cup for 1 hour, at the expiration of which time the test flame must again be applied.

If a flash is obtained, the solid mixture will be subject to the provisions of the Petroleum Acts in virtue of this Order.

**NOTE.**—It may in many cases save time in testing samples of petroleum mixtures to apply the test flame after the sample has been a few minutes in the cup and while still at the temperature of the room in which the test is being carried out, provided that the temperature is below 73°F. If a flash is obtained at this means, it is unnecessary to proceed with the test at a higher temperature.

In 1880 the subject of petroleum testing was investigated in Germany by the Imperial Government, and a considerable number of experiments were made with different forms of apparatus. Eventually the Abel instrument was selected as the best, but exception was taken to the personal error liable to be introduced by the method of applying the test-flame, and accordingly a clockwork arrangement for moving the test-slide and bringing the igniting flame to the required position was added (Fig. 10). The clockwork movement, which is fixed to the cover of the oil cup, is wound up prior to each application of the test-flame, and is released by pressing a trigger as the mercury in the thermometer reaches each  $\frac{1}{2}^{\circ}\text{C}$ . The mechanism is so adjusted that the rate of opening and closing the test-orifice is properly timed, and the operator is therefore relieved from the necessity of timing the movement by the aid of a pendulum. The English Abel-apparatus is provided with both oil-lamp and gas arrangement for igniting the vapour, but the German instrument has the oil lamp only, as it was found that the two appliances did not give in all cases concordant results, and petroleum has advantageously been substituted for colza oil for use in the test-lamp.

Before the Abel tester had been very long in use it was found that the results afforded were materially affected by the amount of atmospheric pressure. This source of variation in flashing-point had not previously received attention, and was first accidentally observed in Germany. As the result of a series of experiments conducted in an air-tight chamber in the Jewish Hospital in Berlin at different atmospheric pressures, it was found that the difference in flashing-point amounted to about 0.30°C. for 10 mm. in the height of the barometric column, and accordingly a table of corrections was framed on this basis for use with the Abel tester in Germany. With the object of procuring some tangible evidence of the effect of barometric changes upon the flashing-point, a series of tests was conducted, in association with the German Government.

Abel, a series of tests at different altitudes in Switzerland, and obtained corroborative results, the observed variations in flashing-point being at the rate of 2°F. for 1 inch of barometric pressure. These experiments

were, however, not made with a view of determining with precision the extent of variation, the number of tests made in the limited time being too few to justify the basing of a table of corrections on the results.

At a later date an additional source of discrepancies in the results afforded by the Abel instrument was discovered in the effect of a tropical temperature upon the liberation of vapour from the oil. The Indian Government, having adopted the Abel apparatus, had copied verbatim from the English Act the directions for applying the test, and attention was forcibly directed to the source of variations alluded to by the condemnation of several cargoes of kerosene, which had arrived in the port of Calcutta. The writer proceeded to India to investigate the matter, and as the result of experiments made in that country and of a series of tests conducted by Sir Frederick Abel and the writer, with the assistance of Dr. Kellner, in an apartment at Woolwich Arsenal heated to a tropical temperature, it was found that a much lower flashing-point than that furnished in a temperate climate was liable to be obtained when the Abel test was applied in a tropical country in the manner prescribed by the English Act. Further experiments made by Dr. Warden, analyst to the Government of Bengal, Professor Pedler of Calcutta, Dr. Lyon, Sir Frederick Abel, Dr. Kellner, and the writer, showed that the apparent depression of the flashing-point was largely due to the vapour which became disengaged in the act of filling the oil cup. Prolonged cooling of the oil appeared to reduce the liability to this disengagement of vapour, but the only practically available method of eliminating this source of discrepancies was found to be the adoption of some expedient for getting rid of the vapour before commencing the operation of testing or before the flashing-point of the oil was reached. Various methods of effecting this object were tried. The vapour was easily removed by gently blowing over the surface of the oil before placing the cover on the cup, or by the use of an aspirator attached to the cover, or by leaving the test-slide withdrawn for some time; but it was ultimately decided to recommend the commencement of the test many degrees below the flashing-point, so that the disengaged vapour might be removed by the current of air created by the test-flame in successive quantities too small to cause a flash before the active volatilisation of the oil began. With this modification in the method of applying the test in a tropical country, the apparatus is caused to give results which agree very closely with those which it furnishes in a temperate climate. Obviously, a portion of the volatile constituents of the oil becomes dissipated in this mode of conducting the test, but, since kerosene cannot be exposed to the air in the tropics without this loss occurring, the defect is not of practical importance. Further details in regard to this question will be found in a joint communication by Sir Frederick Abel and the writer published in the Chemical News on May 2, 1884. In October, 1887, Sir Frederick Abel drew up the following instructions for the use of the Abel tester in temperate and tropical climates:—

*Directions for preparing and using apparatus for testing petroleum oil* (these directions apply

to the use of the Abel tester in temperate climates):—

1. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow pipe. The temperature of the water at the commencement of each test, as indicated by the long-bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in the vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication, or the water is heated by a spirit lamp (which is attached to the stand of the apparatus) until the required temperature is reached.

2. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton-wool moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted the flame is adjusted until it is the size of the bead fixed on the cover of the oil-cup.

3. *Filling the oil-cup.*—The oil-cup is placed on a level surface in a good light, and the oil to be tested is poured in without splashing, until its surface is level with the point of the gauge which is fixed in the cup. The oil should be poured from a suitable small vessel, never direct from a large can. The round-bulb thermometer is inserted into the lid of the cup, care being taken that the projecting rim of the collar touches the edge of the socket; the test-lamp, prepared as already described, is placed in position, and the cover put on to the cup and pressed down so that its edge rests on the rim of the cup.

4. *The application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the test-flame being compared with that of the bead on the cover. The cup is carefully lifted without being shaken, placed in the bath, and the test-lamp lighted. The thermometer in the oil-cup is now watched, and when the temperature has reached 66°F. (the sample, if necessary, having previously been cooled to below that temperature by immersing the vessel containing it in cold water), the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree.

If the oil-cup is fitted with the automatic (Pensky's) arrangement, the opening and shutting the slide, the clockwork is wound up by turning the knob from left to right, and set in motion by pressing the trigger.

If the slide is intended to be moved by hand, it should be drawn open slowly and shut quickly. The exact time to be observed in this operation is regulated by the swing of the pendulum supplied with this form of instrument. The opening of the slide should take the time of three oscillations, the shutting of the slide the time of the fourth oscillation of the pendulum. (By one oscillation is meant the passage of the ball of the pendulum from the greatest distance from

the vertical on the one side, to the greatest distance on the other.)

If a flash occurs at the first application of the test-flame (at 66°F.), or at any point below 73°F., the operation is to be repeated with a fresh portion of the oil, which is cooled down to 55°F. before being placed in the cup. The first application of the test-flame is made when the temperature of the oil has reached 60°F.

In repeating a test, a fresh sample of oil must always be used, the tested sample being thrown away.

**5. Correction for atmospheric pressure.**—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1.6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended (see table following the directions for applying the test in hot climates), giving the flashing-points of oils ranging from 65°–80°F., under pressures ranging from 27–31 inches of mercury.

The table is used in the following manner:—

**Example.**—An oil has given a flashing-point of 71°, the barometer being 28.6; take the nearest number to 71° in the vertical column headed 28.6. This number is 70.8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of barometer). The substituted number, i.e. the true flashing-point of the oil, is 73°.

The following directions apply to the use of the Abel Petroleum Tester in hot climates.

*Directions for drawing the sample and preparing it for testing.*

**1. Drawing the sample.**—In all cases the testing officer, or some person duly authorised by him, shall personally superintend the drawing of the sample from an original . . . . . other vessel.

An opening sufficiently large to admit of the oil being rapidly poured or siphoned from the tin or other vessel shall be made.

Two bottles, each of the capacity of about forty fluid ounces, are to be filled with the oil. One of these, the contents of which is intended to be preserved for reference in case of need, is to be carefully corked, the cork being well driven home, cut off level with the neck, and melted sealing-wax worked into it. The other bottle may be either stoppered or corked.

**2. Preparing the sample for testing.**—About ten fluid ounces of the oil, sufficient for three tests, are transferred from the bottle into which the sample has been drawn to a pint flask or bottle, which is to be immersed in water artificially cooled until a thermometer, introduced into the oil, indicates a temperature not exceeding 50°F.

*Directions for preparing and using the test apparatus.*

**3. Preparing the water-bath.**—The water-bath is filled by pouring water into the funnel

until it begins to flow out at the overflow-pipe. The temperature of the water at the commencement of each test, as indicated by the long bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or the water is heated by means of a spirit-lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

**4. Preparing the test-lamp.**—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton wool, moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted, the wick is adjusted by means of a pair of forceps, or a pin, until the flame is the size of the bead fixed on the cover of the oil-cup; should a particular test occupy so long a time that the flame begins to get smaller, through the supply of oil in the lamp becoming exhausted, three or four drops of petroleum are allowed to fall upon the tuft of wool in the lamp from the dropping bottle or pipette provided for the purpose. This can be safely done without interrupting the test.

**5. Filling the oil-cup.**—Before the oil-cup is filled, the lid is to be made ready for being placed upon the cup, i.e. the round-bulb thermometer is to be inserted into the socket (so that the projecting rim of the collar with which it is fitted touches the edge of the socket), and the test-lamp is to be placed in position. The oil-cup, having been previously cooled by placing it bottom downwards in water at a temperature not exceeding 50°F., is now to be rapidly wiped dry, placed on a level surface in a good light, and the oil to be tested is poured in without splashing until its surface is level with the point of the gauge which is fitted in the cup. The lid is then put on the cup at once, and pressed down so that its edge rests on the rim of the cup.

**6. Application of the test.**—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the entire test-flame being compared with that of the bead on the cover. The cup is carefully lifted, without shaking it, and placed in the bath, the test-lamp is lighted, and the clockwork wound up by turning the key. The thermometer in the oil-cup is now watched, and when the temperature has reached 56°F. the clockwork is set in motion by pressing the trigger.

If no flash takes place, the clockwork is at once re-wound, and the trigger pressed at 57°F. and so on, at every degree rise of temperature, until the flash occurs, or until a temperature of 95°F. has been reached.

If the flash takes place at any temperature below 77°F. the temperature at which it occurs is to be recorded. The fresh portions of the sample are then to be successively tested in a similar manner and the results recorded. If no greater difference than 2°F. exists between any

two of the three recorded results, each result is to be corrected for atmospheric pressure, as hereafter described, and the average of the three corrected results is the flashing-point of the sample. In the event of there being a greater difference than 2°F. between any two of the results, the series of tests is to be rejected, and a fresh series of three similarly obtained, and so on until a sufficiently concordant series is furnished, when the results are to be corrected and the average taken in the manner already described.

No flash which takes place within eight degrees of the temperature at which the testing is commenced shall be accepted as the true flashing-point of the sample tested. In the event of a flash occurring at or below 64° when the test is commenced in the manner above described the next test is to be commenced ten degrees lower than the temperature at which the flash had been previously obtained—that is to say, at 54° or thereunder, and this procedure shall be continued until the results of three consecutive tests do not show a greater difference than 2°.

If a temperature of 76°F. has been reached without a flash occurring, the application of the test-flame is to be continued until a temperature of 95°F. has been reached. If no flash has occurred up to this point, and if the petroleum is declared to be imported subject to the provisions of the Act,<sup>1</sup> the tests shall not be continued, and the testing officer shall certify that the petroleum has a flashing-point of over 95° and is not dangerous. But if the petroleum is oil ordinarily used for lamps, or is declared to have its flashing-point at or above 200°, or is oil to which the provisions of the Governor in Executive Council exempting it from the operation of the Act will be applicable in the event of its flashing-point being found to be at or above 95°. The test shall be continued as follows:—The oil-cup is to be removed from

the water-bath, and the temperature of the water in the water-bath is to be reduced to 95°F. by pouring cold water into the funnel (the hot water escaping by the overflow pipe). The air-chamber is then to be filled to a depth of 1½ inches with water at a temperature of about 95°F., the oil-cup is to be replaced in the water-bath, and the spirit-lamp, attached to the water-bath, is to be lighted and placed underneath. The test-flame is then to be again applied from 96°F., at every degree rise of temperature as indicated by the thermometer in the oil-cup until a flash takes place, or until a temperature of 200°F. or 120°F., as the case may be, has been reached. If during this operation the test-flame appears to diminish in size, the lamp is to be replenished in the manner prescribed (at 4) without interrupting the test.

If a flash occurs at any temperature between 76° and 200°F., the temperature at which it occurs, subject to correction for atmospheric pressure, is the flashing-point of the sample.

In repeating the test on a sample of oil must always be used, the tested sample being thrown away, and the cup must be wiped dry from any oil which may have cooled, as already described, and the fresh sample.

7. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1.6°F. for every inch of the barometer, a correction of the observed flashing-point becomes necessary. The correction must, therefore, be determined at the time of making the test for each sample. If an aneroid barometer is used, the correction may be determined by consulting the following table. To facilitate the correction for pressure a table is given of the flashing-points of oils ranging from 27 to 31 inches of mercury.

The table is used in the following manner:—

TABLE FOR CORRECTION OF FLASHING-POINTS INDICATED BY THE TEST FOR VARIATIONS IN BAROMETRIC PRESSURE ON EITHER SIDE OF THIRTY INCHES.

Barometer in inches.																				
27.0	27.2	27.4	27.6	27.8	28.0	28.2	28.4	28.6	28.8	29.0	29.2	29.4	29.6	29.8	30	30.2	30.4	30.6	30.8	31.0
Flashing Point in Degrees Fahrenheit.																				
60.2	60.5	60.8	61.2	61.5	61.8	62.1	62.4	62.8	63.1	63.4	63.7	64.0	64.4	64.7	65	65.3	65.6	66.0	66.3	66.6
61.2	61.5	61.8	62.2	62.5	62.8	63.1	63.4	63.8	64.1	64.4	64.7	65.0	65.4	65.7	66	66.3	66.6	67.0	67.3	67.6
62.2	62.5	62.8	63.2	63.5	63.8	64.1	64.4	64.8	65.1	65.4	65.7	66.0	66.4	66.7	67	67.3	67.6	68.0	68.3	68.6
63.2	63.5	63.8	64.2	64.5	64.8	65.1	65.4	65.8	66.1	66.4	66.7	67.0	67.4	67.7	68	68.3	68.6	69.0	69.3	69.6
64.2	64.5	64.8	65.2	65.5	65.8	66.1	66.4	66.8	67.1	67.4	67.7	68.0	68.4	68.7	69	69.3	69.6	70.0	70.3	70.6
65.2	65.5	65.8	66.2	66.5	66.8	67.1	67.4	67.8	68.1	68.4	68.7	69.0	69.4	69.7	70	70.3	70.6	71.0	71.3	71.6
66.2	66.5	66.8	67.2	67.5	67.8	68.1	68.4	68.8	69.1	69.4	69.7	70.0	70.4	70.7	71	71.3	71.6	72.0	72.3	72.6
67.2	67.5	67.8	68.2	68.5	68.8	69.1	69.4	69.8	70.1	70.4	70.7	71.0	71.4	71.7	72	72.3	72.6	73.0	73.3	73.6
68.2	68.5	68.8	69.2	69.5	69.8	70.1	70.4	70.8	71.1	71.4	71.7	72.0	72.4	72.7	73	73.3	73.6	74.0	74.3	74.6
69.2	69.5	69.8	70.2	70.5	70.8	71.1	71.4	71.8	72.1	72.4	72.7	73.0	73.4	73.7	74	74.3	74.6	75.0	75.3	75.6
70.2	70.5	70.8	71.2	71.5	71.8	72.1	72.4	72.8	73.1	73.4	73.7	74.0	74.4	74.7	75	75.3	75.6	76.0	76.3	76.6
71.2	71.5	71.8	72.2	72.5	72.8	73.1	73.4	73.8	74.1	74.4	74.7	75.0	75.4	75.7	76	76.3	76.6	77.0	77.3	77.6
72.2	72.5	72.8	73.2	73.5	73.8	74.1	74.4	74.8	75.1	75.4	75.7	76.0	76.4	76.7	77	77.3	77.6	78.0	78.3	78.6
73.2	73.5	73.8	74.2	74.5	74.8	75.1	75.4	75.8	76.1	76.4	76.7	77.0	77.4	77.7	78	78.3	78.6	79.0	79.3	79.6
74.2	74.5	74.8	75.2	75.5	75.8	76.1	76.4	76.8	77.1	77.4	77.7	78.0	78.4	78.7	79	79.3	79.6	80.0	80.3	80.6
75.2	75.5	75.8	76.2	76.5	76.8	77.1	77.4	77.8	78.1	78.4	78.7	79.0	79.4	79.7	80	80.3	80.6	81.0	81.3	81.6

<sup>1</sup> The Indian Petroleum Act is here referred to.

*Example.*—An oil has given a flashing-point of  $71^{\circ}$ , the barometer being at 30.0, nearest number to  $71^{\circ}$  in the vertical column headed 28.6. This number is 70.8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of the barometer). The substituted number, *i.e.* the true flashing-point of the oil, is  $73^{\circ}$ .

'Dangerous petroleum' is defined by the Indian Petroleum Act as 'petroleum having a flashing-point below  $76^{\circ}$  of Fahrenheit's thermometer. Provided that, when all or any of the petroleum on board a ship, or in possession of a dealer, is declared by the master of the ship or the consignee of the cargo, or by the dealer, as the case may be, to be of one uniform quality, the petroleum shall not be deemed to be dangerous if the samples selected from the petroleum have their flashing-points, on an average, at or about  $73^{\circ}$  of Fahrenheit's thermometer, and if no one of those samples has its flashing-point below  $70^{\circ}$  of that thermometer.'

The Abel apparatus, with a standard of  $22^{\circ}\text{C}$ ., was in 1885 adopted as the legal test in Sweden, and in the year 1888 a Bill was introduced in the British Parliament to substitute



FIG. 11.

with a standard of  $23^{\circ}\text{C}$ ., for the open tester, with a standard of  $40^{\circ}\text{C}$ ., then in use in Denmark. In Russia the standard with the Abel-Pensky instrument is  $28^{\circ}\text{C}$ .

The Abel tester is by no means the only form of closed testing apparatus at present in use, and, in addition to those actually employed, a large number of instruments on the closed-cup principle have been devised. Many years ago Tagliabue, of New York, introduced an apparatus (Figs. 11 and 12) with a covered brass oil cup communicating by means of a spring valve with a

dwarf chimney. The opening of the valve and the simultaneous introduction of a flame into the chimney determines a current of air through the upper part of the oil-cup which sweeps out the inflammable vapour and brings it into contact with the flame. Tagliabue also constructed a larger instrument of the same form with a glass oil-cup. The Michigan and Wisconsin States tester has a copper oil cup with a copper cover provided with a small orifice to which the test flame is applied. The New York State tester, devised by Elliott, has a glass oil-cup of comparatively large size with a convex glass cover. Parrish's naphthometer (Fig. 13) is provided with a stationary test flame fed by the oil in the testing cup, and Foster's automatic tester (Fig. 14) is similar in principle. In Millspaugh's closed tester (Fig. 15) the oil-cup is of glass and is immersed only to the extent of one-tenth of its depth in the water-bath, with the object, apparently, of preventing the overheating of the surface of the oil. Mann's tester (Fig. 16) represents an attempt to reproduce in the testing apparatus the conditions prevailing in an ordinary petroleum lamp, the burner of the

lamp being replaced by a tube, the stopper of which is blown out when, upon the introduction of a light through a lateral opening, ignition of

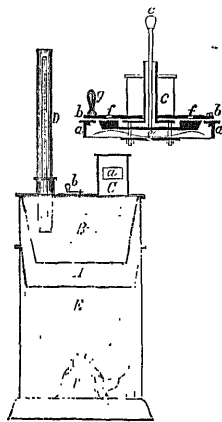


FIG. 12.

The smaller illustration represents in section the cover of Fig. 11. *a, a*. Cover. *b, b*. Cover, closed by the bar *e*. *c*. Rod to depress the bar *e*, and thus uncover the openings *f, f*. *g*. Handle to move the bar *b, b*. *d*. Hood with opening for insertion of flame.

The larger illustration represents in section a simpler form of the instrument. *A*. Water-bath. *B*. Oil-cup. *c*. Hood, with opening *a*. *D*. Thermometer. *E*. Lamp furnace. *F*. Lamp. *b*. Pivoted cover, closing orifice beneath it.

the vapour occurs. In Pease's closed tester (Fig. 17) the vapour is ignited by an electric-spark. The writer remembers seeing, about

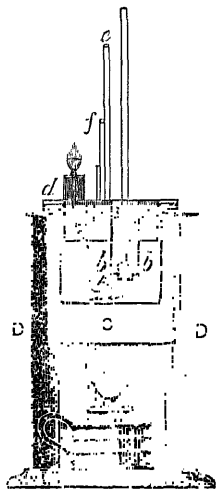


FIG. 13.

*A*. Oil-cup. *C*. Water-bath. *D*. Lamp-furnace. *e*. Screen, with glass plate *f*. *B*. Chamber communicating with the air, with openings *a* (for circulation of air) and *b, b* (to allow passage of oil from *B* into *A*). *d*. Cylinder supporting a small wick for test flame.

the year 1870, a closed tester, with electric-spark igniting arrangement, in use by Dr. Lethby in his laboratory at the London Hospital. The

oil-cup was of glass, with a hinged metal cover, which was blown open when the vapour ignited. In 1882, Braun, of Berlin, patented a magnetic pendulum arrangement for applying the test flame in the Abel apparatus. In 1881, Engler

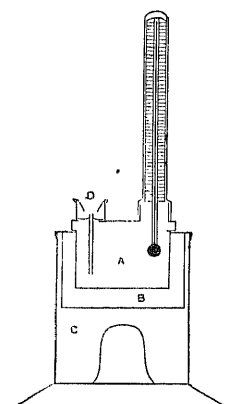


Fig. 14.

A. Oil-cup. B. Water-bath. C. Jacket. D. Flash-jet.

and Haas made a number of experiments with the Abel apparatus and other testing instruments, and expressed the opinion that the addition of an arrangement for agitating the oil was desirable; and, however, previously proposed, of a stirrer. Owing to the facts that in the use of the Abel tester a layer of vapour of gradually increasing

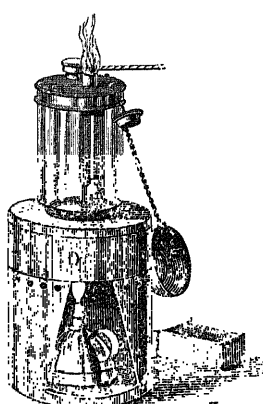


Fig. 15.

thickness is formed upon the surface of the oil and that the temperature of the oil is not uniform throughout, it is, no doubt, necessary that the dimensions of the air space above the oil, the depth to which the test-flame is inserted, the size of the test-flame, the size of the orifices in the cover, the position of the thermometer bulb, and other particulars, should be defined with greater accuracy than would probably be necessary if a stirrer were added, but experience has shown that the Abel apparatus can be readily standardised, and any number of instru-

ments can thus be constructed to give concordant results if used with a reasonable amount of care. The apparatus known as the Engler tester (Fig. 18) consists of a copper water-bath surmounted by a second water-bath of glass

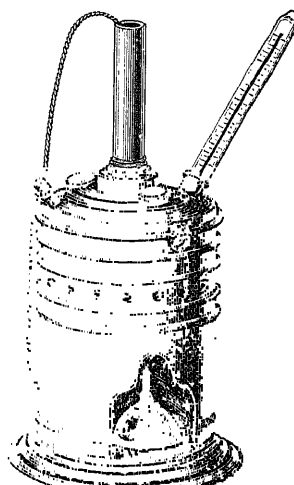


Fig. 16.

supporting a glass oil-cup with brass cover in which are two semi-circular openings with hinged lids. Two insulated wires in connection with a small induction coil terminate in platinum points 1 mm. apart at a distance of  $\frac{1}{2}$  to  $\frac{3}{4}$  cm. from the surface of the oil, and in the centre of the oil-cup is a paddle stirrer attached to a spindle passing through the cover. Beneath the

lower water-bath a spirit lamp is placed, and, as the temperature approaches the flashing-point of the oil, the spark is passed at each degree rise in the thermometer, care being taken that the passage of the spark is continued from half to one second. After each application of the spark the oil is gently agitated by rotating the stirrer.

It is claimed that by the use of the double water-bath and the stirrer the heating is rendered slow and regular, and as far as possible independent of the size of the heating flame; also that by the employment of the electric spark, the size, intensity, and distance of the test-flame from the oil are rendered constant, so that the extraneous formation of vapour through the heating of the surface of the oil which may take place when an ordinary test-flame is employed cannot occur in the use of the electric spark as described. Finally it is contended that the

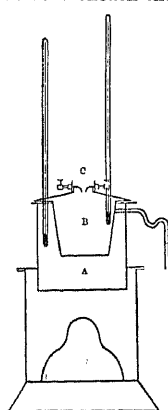


Fig. 17.

A. Water-bath. B. Oil-cup. C. Spark wires.

conditions prevailing in a petroleum lamp are reproduced to a large extent in the Engler tester.

Among other systems of testing are those of Liebermann, Beilstein, and Stoddard, which are

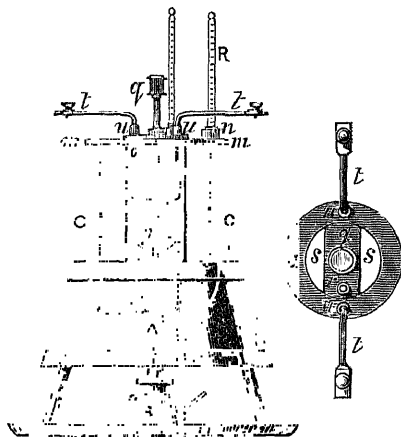


FIG. 18.

A. Copper water-bath. B. Spirit lamp. C, C. Glass water-bath, with filling mark etched upon it. *m, m*. Cover. R. ... by collar *n*. ... *s, s*. ... wires, insulated by ebony rings *u, u*, and terminating in platinum points. *p*. Stirrer, with handle *q*. *r*. Thermometer in the oil.

based upon the principle of blowing air at intervals through a jet plunged beneath the surface of the oil, contained in a vessel in which it can be gradually heated, until inflammable vapour is evolved. In Bernstein's tester (Fig. 19)

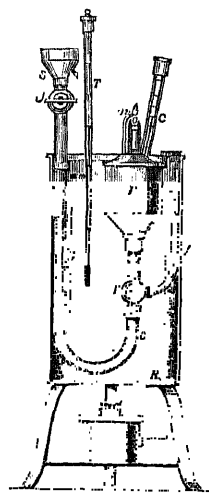


FIG. 19.

a cylindrical chamber B, a graduated tube *m*, 35 cm. in length, and a thermometer. The cylindrical chamber is closed

at the top by a screw-plug *p*, and at the bottom by a sliding plate, which cuts off communication between the chamber and the vessel below. 50 c.c. of water having been placed in the lower vessel, the cylindrical chamber is nearly filled with the petroleum to be tested, the screw-plug replaced, and the apparatus

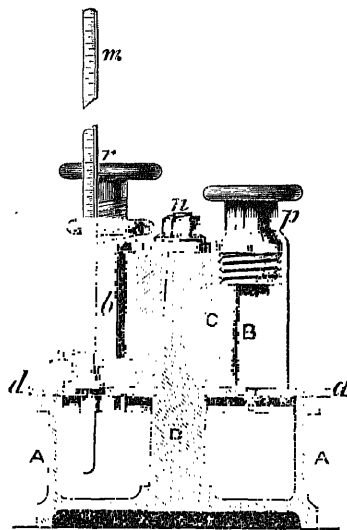


FIG. 20.

placed in warm water until the temperature has become constant. The water-level in the graduated tube having been adjusted to zero by means of the regulating screw, the oil in the cylindrical chamber is caused to flow out upon the surface of the water in the lower vessel by moving the sliding plate. The expansion of the liberated vapour of the petroleum causes the water to rise in the graduated tube, and, when the level is ... read off. In a table published by Salleron and Urbain give the following figures of sp.gr. and vapour tension of petroleum at 15°:

Density at 15°C.	Tension in mm. of water	Density at 15°C.	Tension in mm. of water
0.812	0	0.756	125
0.797	5	0.735	410
0.788	15	0.695	930
0.772	40	0.680	1185
0.762	85	0.650	2110

In regard to the Salleron-Urbain system of testing, Engler and Haas remark that the method depends upon the assumption that the numbers which express the expansion of the petroleum vapour are parallel with the ... all kinds of petroleum; but that the supposition is found not to be correct in all cases, inasmuch as the presence of a small quantity of very volatile hydrocarbons occasions an increased pressure in the apparatus. The general conclusion is, however, expressed that oils which exhibit a tension of not more than 64 mm. of water at 35° may be considered safe.

Presumably a quantity too small to sensibly affect the inflammability.

In a report to the New York State Board of Health in 1882, Professor Arthur H. Elliott records the particulars of a large number of experiments with various forms of testing apparatus, and gives the following table of comparative results:—

Oil used.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Flashing-points, F.										
No. 1 . . .	110°	118°	120°	111°	117°	107°	103°	130°	111°	95°	119°
No. 2 . . .	111°	121°	124°	115°	118°	109°	102°	128°	107°	96°	—
No. 3 . . .	119°	122°	122°	112°	118°	108°	102°	130°	108°	95°	118°
No. 4 . . .	97°	96°	97°	90°	93°	86°	76°	90°	81°	75°	96°

I. Tagliabue (open cup). II. Arnaboldi (open cup). III. Saybolt. IV. Tagliabue (closed cup—small). V. Tagliabue (closed cup—large). VI. Wisconsin State. VII. Abel. VIII. Bernstein. IX. Millsbaugh. X. Mann. XI. Foster.

From the statements which have been made it will be evident that there is a regrettable absence of uniformity in the methods of testing adopted, not only in different countries, but also in the various States of the American Union. The existence of considerable diversity in regard to the test standard to be adopted with any one system of testing is also exhibited in the laws which have been framed in the United States. The latter condition no doubt arises from the fact that, at the outset, no systematic attempts were made to determine the relation between the flashing-point of an oil and its safe or dangerous character in ordinary use.

(e) *Burning quality.*—The testing of the burning quality of kerosene is regularly effected

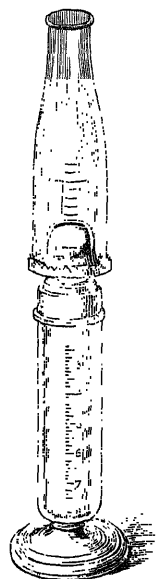


FIG. 21.

of the flame and the depression of the oil level being noted.

In Canada the 'burning percentage' is determined by the use of a lamp thus described: 'The bowl of the lamp is cylindrical, 4 in. in diameter and 2½ in. deep, with a neck placed thereon of such a height that the top of the

wick tube is 3 in. above the bowl. A sun hinge burner is used, taking a wick ¾ in. wide and ¼ in. thick, and a chimney about 8 in. long.' The test is conducted as follows: 'The lamp bowl is filled with the oil and weighed, then lighted and turned up full flame, just below the smoking point, and burned without interference till 12 oz. of the oil is consumed. The quantity consumed during the first hour and the last hour is noted.' The ratio of the two quantities is the measure of the burning quality, and the percentage that the latter quantity is of the former is the 'burning percentage' referred to.

The writer has devoted much time to the perfecting of a system of testing burning quality with lamps of the usual construction, and has succeeded in eliminating some of the sources of discrepancies in the results afforded. Obviously the wick used should be carefully chosen, and, as a fresh wick should be employed for each test, it is important that the wick should be examined before use, and any defective portion rejected. In standardising the wick and verifying its uniformity, the writer has found it advantageous to determine the quantity of a mineral oil of known quality drawn out of a vessel by the capillary attraction of a piece of the wick, dried immediately before use and immersed in the oil while still warm. The oil chambers of the lamps employed must be of uniform dimensions, and the burners must first be tested to ascertain that they furnish similar flames with the same oil. The wick must be trimmed with scrupulous care before the lamp is lighted, and the oil in the lamp must be maintained at a constant temperature—that of 60°F. being a desirable one. The wick should be raised so as to obtain a flame of the largest size possible without the production of smoke. For recording the size and shape of the flame at the commencement of the experiment and the diminution in size and alteration in shape of the flame at intervals during the progress of the test, the writer has found it convenient to employ a camera by means of which the outline of the flame may be traced on thin paper at intervals (Fig. 23). No general agreement has, however, yet been arrived at as to the extent of diminution which shall, under the specified conditions, be permissible with oils to be classed as of satisfactory burning quality. In doubtful cases several tests of the sample should be made,



as the results appear to be sometimes affected by causes not well understood. In consequence of the difficulty of devising a thoroughly satisfactory method of testing oils by burning, it has been proposed to establish a distillation test, the inferiority in burning quality being supposed to

or in the Mahler bomb, and the sulphur products estimated as barium sulphate.

#### 4. Lighthouse oil.

The Trinity House contract conditions for mineral oil intended for use in lighthouse lamps specify that—

(1) The mineral oil required to be supplied under this contract is to be of the best possible quality, the greatest care is to be taken in its preparation, and it must be perfectly free from sulphuric acid.

(2) In all cases, whether the oil be petroleum or paraffin, its flashing-point is to be determined by using the apparatus described in Schedule 1 of the Petroleum Act of 1879.

(3) If the oil be petroleum, its flashing-point is to be not lower than 125°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(4) If the oil be paraffin, its sp.gr. is to be not less than 0.810, nor greater than 0.820, at 60°F.; its flashing-point is to be not lower than 140°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(5) The illuminating power of the oil supplied, whether petroleum or paraffin, is to be equal to that of the best colza oil when consumed in a Trinity House Argand lamp.

For the distillation test about 250 grams of the oil may be taken, the operation being conducted in an ordinary distillation flask with the bulb of the thermometer midway between the shoulder of the flask and the lateral tube leading to the condenser. The upper part of the flask should be wrapped in asbestos cloth.

The United States Lighthouse establishment stipulates that mineral oil supplied for use in lighthouse lamps shall have a sp.gr. 'not less than 0.802,' a flashing-point of not less than 140°F., and a fire-test of not less than 154°F., both these tests being made with Tagliabue's instrument. The oil is to remain limpid at zero; and 'litmus paper immersed in it for 5 hours must remain unchanged.' The oil is to be photometrically tested in a fifth-order Hains lamp, and the light is to be equal to that of eighteen sperm candles, and to continue undiminished during 5 hours' burning.

#### 5. Lubricating oils.

*a. Colour.* In the case of what are known as pale oils, the trade are accustomed to take exception to any marked increase in the ordinary depth of colour, but as yet there are no accepted standards of colour for these oils, such as have been fixed for kerosene. The writer has, however, for some years past, used the instrument (Fig. 24) known as Lovibond's Tintometer<sup>1</sup> in ascertaining and recording the colour of a two-inch column of lubricating oils, and compar-

This instrument, devised by Mr. Joseph W. Lovibond, of Salisbury, consists of a covered trough or box partitioned by a vertical plate, the partition terminating in a glass eye-piece fixed at one end, and at the other end a glass plate slightly diverging from the end at which the eye-piece is placed. In one channel the liquid to be examined, which is contained in a rectangular glass cell, is placed; and in the other channel numbered slips of coloured glass, of known depth of tint, are inserted.

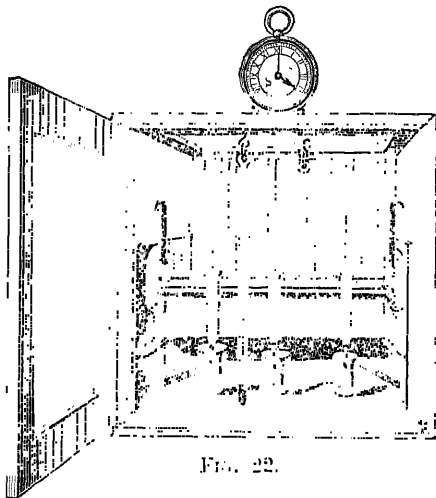


FIG. 22.

arise from the oil not being of natural composition or from its containing too large a percentage of the denser hydrocarbons. Attempts in this direction have not, however, been attended with success, oils of different burning quality furnishing in some cases similar results, and oils of equally good burning quality sometimes giving dissimilar results on fractional distillation. The testing of the oil under conditions as nearly as possible approaching to those under which it is practically used appears to be the most rational method of determining the burning quality, and is no doubt the best in the absence of any arbitrary test capable of being easily and expe-

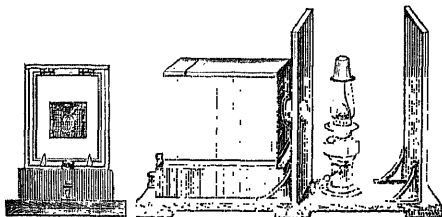


FIG. 23.

ditiously applied and of furnishing trustworthy results. The viscosity of the oil has been found in some cases to afford a useful indication of burning quality.

Kerosene oil should bear agitation with oil of vitriol without material darkening of colour, and warm water shaken with it should exhibit neither markedly alkaline nor even faintly acid reaction, and should give no precipitate with a barium chloride solution. Upon burning, kerosene should not evolve sulphur compounds; the presence of any considerable amount of sulphur compounds is suspected, the oil should be burned in a Referee's gas-testing apparatus,

tive results have thus been furnished for the guidance of the trade.

b. *Cold-test.* Lubricating oils should be free from such odour, as the presence of such odour would indicate that the process of refining had not been satisfactorily carried out.

c. *Specific gravity.* Mineral lubricating oils of *heavy* grade were formerly graded

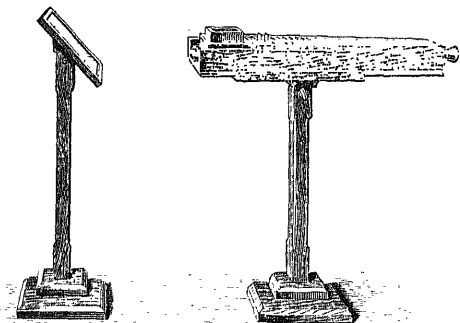


FIG. 24.

solely with reference to specific gravity, but, experience having shown that the density is not necessarily an index of the lubricating value, it is now generally recognised that specific gravity is a less reliable criterion than viscosity.

d. *Fire-test.* The determination of the fire-test, the writer is accustomed to use an instrument made by Pensky of Berlin. In its closed form this apparatus resembles in principle the Abel tester employed in the examination of kerosene. The water-bath is, however, replaced by an air-bath, consisting of a thick cast-iron vessel which is heated by a Bunsen burner, and the application of the gas test-flame is effected through the medium of a revolving vertical spindle with a *test-cup* which can be grasped by the *operator* without inconvenience even when the apparatus is used at high temperatures. In the use of this instrument the flame of the burner should be adjusted so that the temperature of the oil rises at the rate of about 10°F. per minute. The latest form of the apparatus, known as the Pensky-Martens tester (Fig. 25), is provided with a revolving stirrer which agitates the atmosphere above the oil as well as the oil itself.

If the cover of the oil-cup be removed, the apparatus referred to may be employed for the determination of the open-vessel flashing-point and the fire-test, a gas flame, not more than  $\frac{1}{4}$  inch in diameter, being used to produce the ignition.

Inspectors of lubricating oils in the United States commonly use in ascertaining the fire-test an open metallic cup, supported on a tripod stand and heated directly by the flame of a spirit lamp, the temperature being raised at the rate of eight degrees Fahrenheit per minute.

In some cases it is customary to test the volatility of the oil by noting the loss of weight sustained by a given quantity of the oil when exposed for a given time to an elevated temperature. The oil is

sometimes absorbed by filter-paper before exposure to heat.<sup>1</sup>

e. *Cold-test.* The method in which the 'cold-test' of lubricating oils is made varies with the description of oil, and to some extent with the interpretation which the operator places on the term. The cold-test of pale oils is usually accepted as being the point at which on a gradual reduction in the temperature separation of solid hydrocarbons commences. To some descriptions of pale lubricating oils the following 'cold-test,' which may be termed the 'cloud-test,' is applied in the writer's laboratory: A beaker about 3 ins. in height by  $1\frac{1}{2}$  ins. in diameter, is filled to a depth of 1 in. with the oil to be tested. The oil is slowly cooled, and from time to time is gently stirred with a thermometer until the first indication of the separation of paraffin is observed. This indication often takes the form of a cloudy stream following the thermometer as it is slowly moved. Some of the more viscous pale oils contain hydrocarbons which are not very crystalline, but which incline rather than paraffin wax, at which these hydrocarbons begin to separate under the influence of cold is not easily determined. In some of such cases it is preferable to take the point at which the

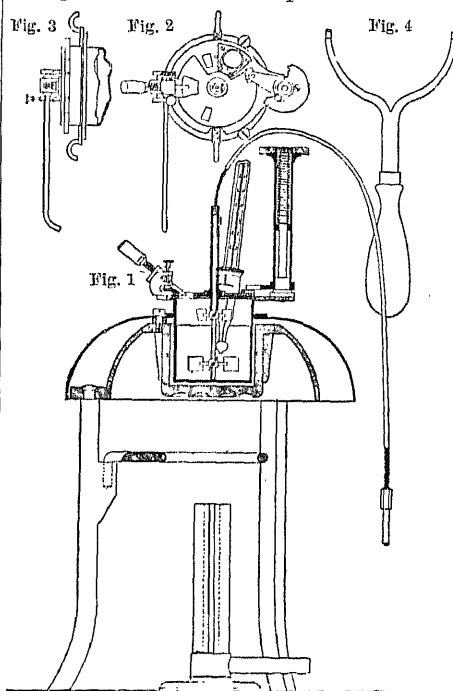


FIG. 25.

Fig. 1. Apparatus with test-flame in position for igniting the vapour. Fig. 2. Cover of oil-cup. Fig. 3. Side view of cover. Fig. 4. Handle for removing oil-cup from bath when hot.

oil becomes reduced to a semi-solid consistency or ceases to flow on inclining the vessel in which

<sup>1</sup> The writer is accustomed to expose 25 grams for 12 hours to 150°F. in the case of

it is contained. In all cases it is important that the temperature of the bath employed for cooling should not be much lower than that at which the separation, or solidification, occurs, and it is therefore desirable to determine approximately the cold-test by a preliminary operation. Where the separation of solid hydrocarbons is well defined, the test may be made in a tube about 1 in. in diameter, containing about 1½ ins. in depth of oil in the following manner: Plunge the tube into a vessel of iced water, or, if necessary, into ice and salt, until a thin layer of paraffin congeals on the sides, stirring the oil with a thermometer while the reduction of temperature is being effected. Take out the tube, wipe it, and holding it between the operator and the window, stir the contents with a thermometer until the last traces of paraffin have disappeared, when the temperature is to be noted. Repeat the experiment, again noting the temperature. Make a third test, and if the results of the last two experiments agree, record this temperature as the cold-test of the sample.

Black oils are tested by cooling them until they cease to flow, as the commencement of the separation of solid hydrocarbons cannot be observed in these oils.

The rules of the New York Produce Exchange provide that the cold-test is to be determined by cooling the sample in a glass vessel, 4 ins. in depth and 3 ins. in diameter, placed in a refrigerator. A thermometer is to be placed with its bulb in the middle of the oil, and another thermometer is to be placed in the ice-chest outside the oil vessel. If, when the two thermometers both record a specified temperature, the oil is still limpid, the cold-test of the oil is deemed to be satisfactory. Tagliabue has devised a convenient form of apparatus (Fig. 26)

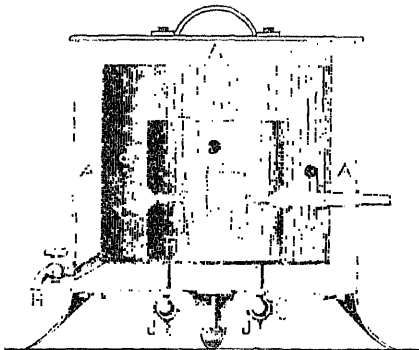


FIG. 26.

A, A, A. Non-conducting jacket. B, C, Ice-chamber. F. Oil-cooling chamber, containing the oil-cup, which is supported on a cooling-stand. H. Top for draining ice-chamber. D, D, D. Thermometers; the central one having its bulb in the oil.

In this test, the oil-cup being placed in a jacketed cooling-chamber with a glass window. In practice, however, the cold-test is usually determined by cooling the oil in a glass cylinder 1½ in. in diameter.

f. *Viscosity.* It has been already stated that this test has become recognised as the proper basis for the grading of lubricating oils, and has accordingly become of considerable importance. The test is necessarily an arbitrary one, and there is at present no universally accepted method of testing and expressing the results, though in this country the Redwood viscometer has been adopted by the War Department, the companies, the Scottish Mineral Oil Association, and the petroleum trade generally. The simplest form of instrument available for the determination of viscosity consists of a glass pipette filled to a mark on the neck and allowed to discharge its contents, the relation between the period occupied in the outflow of a given sample and that required for the discharge of a similar quantity of a standard oil expressing the viscosity of the former sample in terms of the latter. The standard oil of glass pipette is, however,

by the form of the constricted portion of the tube, apart from the size of the orifice, and two pipettes standardised with an oil of a certain viscosity may not afford concordant results with an oil of very different viscosity. Moreover, the maintenance of the required temperature of a sample contained in a glass pipette cannot always be satisfactorily effected. For these reasons the jacketed glass viscometers of Veitch-Wilson, MacIvor, and Sacker have not been found to afford sufficiently accurate results.

The Saybolt viscometer, in its original form (Fig. 27), is provided with an oil vessel of

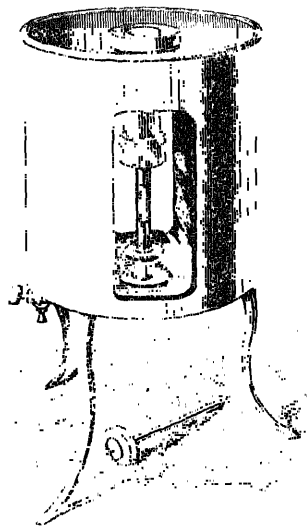


FIG. 27.

comparatively large diameter placed in a water-bath of considerable capacity. The viscometer jet is of metal, and is inclosed in a tube extending below the orifice. Immediately above the jet the oil vessel is much contracted in diameter, and a portion is cut away on each side so as to expose an inner glass tube. At a corresponding level, glass windows are inserted in the water-bath. Round the upper part of

the oil-vessel is fitted an oil-tight gallery with raised edge, and above the platform of the gallery the oil-cylinder is pierced with a number of small holes. In the use of the apparatus, the bath is filled with water at the required temperature, and, a cork having been inserted in the mouth of the tube inclosing the jet, the oil-vessel is filled with the oil to be tested, until overflow through the orifices referred to occurs. The oil is then stirred with a thermometer, the gallery taking the overflow, and its temperature adjusted if necessary. On withdrawing the thermometer, oil passes from the gallery into the oil-vessel to replace that which had overflowed on the insertion of the instrument. The gallery is then emptied by means of a pipette, the length of the oil column being thus determined by the position of the circle of holes; the flow of oil from the jet is started by the withdrawal of the cork from the outer tube; a stop-watch is concurrently set in motion, and the operator, . . . the window in the water-bath . . . glass tube forming the lower part . . . stops the watch when the oil-level makes its appearance.

The Arvine viscometer for testing cylinder oils consists of a copper tube of small diameter coiled in a bath in which water is kept in a state of ebullition. At its lower end the tube is furnished with a small stop-cock, forming a jet, and at its upper end with a funnel to hold the oil.

The Redwood viscometer (Fig. 28) is a modification of the instrument formerly used at the

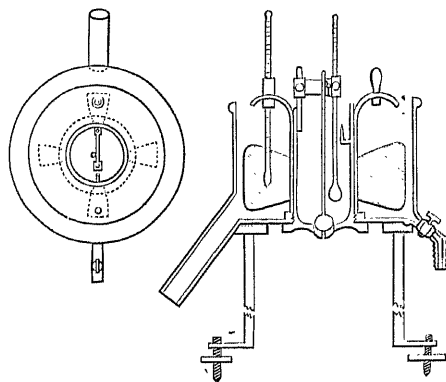


FIG. 28.

Battersea Works of Price's Patent Candle Company. It consists of a silvered copper oil cylinder, about  $1\frac{1}{2}$  ins. in diameter and  $3\frac{1}{2}$  ins. in depth, furnished with an agate jet fitted into a slightly conical metal seating. The cylinder is provided with . . . at an angle of  $45^\circ$  from the side near the bottom, as well as with a revolving agitator carrying a curved shield to prevent splashing, and a thermometer to indicate the temperature of the liquid in the bath. The oil cylinder has a stopper consisting of a small brass sphere which rests in a hemispherical cavity in the agate jet. The sphere is attached to a wire by means of which it is raised and suspended from a standard which supports a thermometer in the oil. Inside the oil-cylinder,

and at a short distance from the top, is fixed a small bracket terminating in an upturned point, which serves as a gauge of the height to which the cylinder is filled. The instrument is supported on a tripod stand. Great care is taken in the construction of the agate jets to secure uniformity, and any slight differences in the rate of flow are corrected by slightly altering the position of the pointed bracket in the oil-cylinder. The instruments are thus all standardised. The viscometer is used in the following manner:—The bath is filled with a suitable liquid to a height . . . the point of the bracket . . . Water may be used for temperatures up to  $200^\circ\text{F}$ ., and a heavy mineral oil for higher temperatures. The liquid being at the required temperature, the oil to be tested, which may previously be brought to the same temperature, is poured into the inner cylinder until its level just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop-watch at the same time started, and the number of seconds occupied in the outflow of 50 c.c. noted. When oils are being tested at a temperature much above that of the laboratory, a gas flame is applied to the heating tube, and the agitator kept in gentle motion throughout the experiment. The maintenance of the exact required temperature of the oil is thus, after a little practice, rendered easy. It is important that the apparatus should stand perfectly level, and that the oil should be free from dirt, water, or other suspended matter. The writer is accustomed to express the results in terms of the viscosity of rape oil at  $60^\circ\text{F}$ ., correcting for differences in specific gravity. Accordingly the number of seconds occupied in the outflow of 50 c.c. of the oil under examination is multiplied by 100 and divided by 535 (the average time occupied in the outflow of 50 c.c. of rape oil at  $60^\circ\text{F}$ . according to the writer's experiments). The result is then multiplied by the sp.gr. of the oil under examination, at the temperature of the experiment, and divided by 915 (the sp.gr. of refined rape oil at  $60^\circ\text{F}$ .).

The writer has devised a modified form of his viscometer, which, with the authority of the Admiralty, will be known as the Admiralty type for testing oil fuel. This instrument, as the name indicates, has been specially constructed for use in determining the viscosity of oil fuel, for contract purposes, and is intended to be employed at a temperature of  $32^\circ\text{F}$ . The oil-vessel is of the same dimensions as that of the original instrument, but the agate jet is longer and of larger bore, the new viscometer being designed to give an outflow in one-tenth of the time occupied in the outflow of a similar volume from the original pattern. The jet is so mounted as to be completely surrounded by the water in the bath. The water-bath, which is of comparatively large size, and is jacketed, has no lateral heating-tube, but is provided with the usual rotating stirrer. The design is registered, and the sole makers are Messrs. Baird & Tatlock (London), Limited. The oil to be tested should be subjected to prolonged cooling at  $32^\circ\text{F}$ . by being kept in a refrigerator

through the night, or for at least six hours, immediately before being placed in the oil-cup, and should be thoroughly stirred before being transferred to the oil-vessel, and when accurate results are required the viscometer should be placed in a refrigerating chamber, the temperature of which is maintained at 32°F.

The Engler viscometer, which is largely used in Germany, is constructed on the same principles as the foregoing, the viscosity of the oil being compared with that of water. The following description of the instrument is taken from the writer's 'Petroleum and its Products' (Griffin), 2nd. ed., 602, 603:—

The apparatus (Fig. 28A) is provided with an oil-cup, A, of brass, closed by a lid, A<sub>1</sub>. The oil-cup is of the dimensions given in the figure, and its inner surface is gilt. In the centre of the convex bottom of the oil-cup is an outflow-tube, a, of platinum (brass being attacked by the oil after being some time in use) 20 mm. long and 2.9 mm. internal diameter at the top, decreasing to 2.8 mm. at the outlet. This tube can be closed by a pointed rod, b, of hard wood, introduced through the lid of the cup. Three small pointed studs, c, turned up at right angles, on the walls of the cup, serve to indicate the surface-level of the oil, marking a capacity of 240 c.c., and also show whether the apparatus is properly adjusted as regards level. A thermometer, t, is inserted in the lid to register the temperature of the oil. The oil-cup is fixed in a bath, B, containing a thermometer, t<sub>1</sub>. The oil-bath is supported by a tripod stand, and is heated by means of a ring burner. A scale, c, marked at 200 c.c. and at 210 c.c., is placed exactly below the pipe, a.

To ensure the attainment of satisfactory results, the dimensions given must be strictly adhered to, for, although the error caused by altering some of them can be corrected, so far as the flow of water at 20°C. is concerned, by varying the length of the pipe, a, the correction is of no value for oils at other temperatures, and the difference in result between such instruments and one of standard dimensions increases with the viscosity of the oil tested.

Every instrument, even when standardised, should be tested before using the first time, and again after having been some time in use, by carefully rinsing out the cup with ether, alcohol, and water, in succession carefully drying the outflow pipe with a strip of filter paper, and observing the time required for the outflow of 200 c.c. of water maintained at 20°C. The water should be quite free from any rotary motion before the vent peg is withdrawn. The time should be 51–53 seconds, and the test should be twice repeated. The difference should not exceed 0.5 second, and the decimals of the average are counted as one second. To test oils, the cup must be most carefully cleansed of all damp and dirt, rinsed with alcohol, ether, and petroleum in succession, and then filled with the oil up to the gauge points. The oil having been brought to the desired temperature by heating the oil-bath, and maintained at that point for 2 or 3 minutes, the peg is withdrawn, and the outflow timed by a good chronometer. The result in seconds, divided by the rate for water at 20°C., gives the viscosity of the oil, e.g.—

Rate of flow of oil, 276 seconds.

„ „ water at 20°C., 53 seconds.

Result=5.2.

Oil containing suspended particles, solid matter, or water, must be filtered or dried before testing.

It has been already stated that in expressing the results obtained with the Redwood viscometer a correction is made for differences in sp.gr. As far as the writer is aware, the first published suggestion of an arrangement for eliminating differences due to sp.gr. was made by Prof. W. P. Mason, of Troy, N.Y., who described in the Chem. News for Oct. 31, 1884, an apparatus

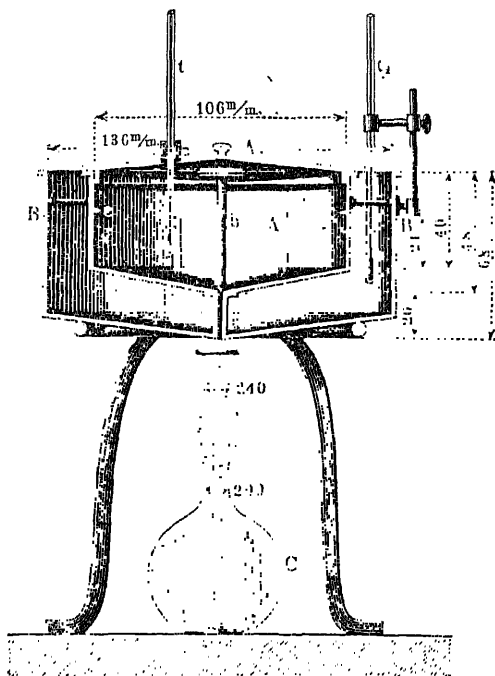


Fig. 28A.

for determining viscosity, and proposed that the length of the column of the oil to be tested should be so adjusted as to be inversely proportional to the sp.gr., and maintained at this calculated length during the outflow of the standard quantity. Mr. Napier, of Glasgow, appears, however, to have previously suggested the reduction of the observed viscosity of an oil to a standard density. In the instrument proposed by Mr. Napier, the oil vessel was in two parts, the upper part being supported in such a manner that it could be placed at a given point on a fixed scale, the height being determined by the sp.gr. of the oil. The movable part of the oil vessel was provided with an overflow pipe, and by the use of a reservoir with a stopcock it was intended to produce a continuous slight overflow, so that the oil-level should be maintained at a fixed point.

The Mason viscometer was thus described:—

A glass cylinder 22 ins. (55.9 cm.) long, 1½ ins. (3.8 cm.) diameter, has a brass lower

head  $\frac{1}{8}$  in. (0.318 cm.) thick. An orifice is bored in the centre  $\frac{1}{32}$  inch (0.794 cm.) in diameter, with bevelled edges, chamfered back  $\frac{1}{8}$  in. (1.27 cm.), thus producing a sharp-edged orifice. A line marking the 18-in. (45.72 cm.) level is cut with several finer lines above and below,  $\frac{1}{8}$  in. (0.318 cm.) apart, ranging from 16 to 21 in. (40.64–53.34 cm.) above the orifice. The standard temperature is usually 60°F. (15.5°C.). A total flow of 6.103 cu. in. (100 c.c.) is recorded by adjusting the supply so that the head shall be as nearly as possible equal to 18 ins. (45.72 cm.) of water, determining this head by calculation from the sp.gr. of the oil. The rule for obtaining the viscosity is to note the time required to discharge the 100 c.c. (6.103 cu. ins.) and divide this time by that required where water under a head of 18 ins. (45.72 cm.) is used. This ratio is the measure of the viscosity.

In the Barbet viscometer the oil under examination is caused to flow through an annular space formed by fixing an iron rod 4 mm. in diameter precisely in the middle of a brass tube 5 mm. in internal diameter. Increased resistance to the flow of the liquid is thus created, and the apparatus is stated to be more sensitive than an ordinary jet viscometer.

Lepenaux' viscometer (Fig. 29) consists of two similar

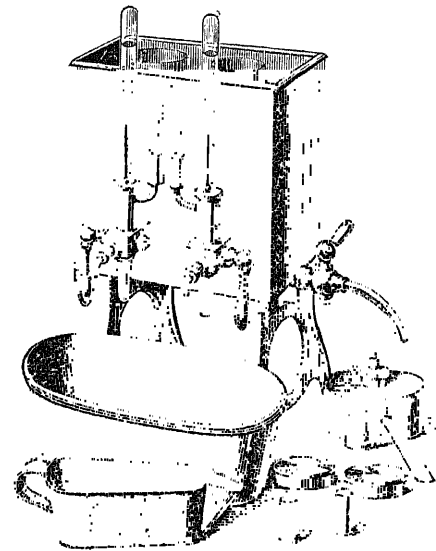


FIG. 29.

side by side in a water-bath, and provided with three pairs of interchangeable jets to be inserted in the ends of the cylinders. A standard oil having been placed in one cylinder, and the oil to be tested in the other, a pair of jets delivering the oil in drops is selected, and the number of drops falling from the two cylinders between two coincidences of dropping is noted. With dissimilar oils, however, the number of drops is not necessarily a measure of the quantity flowing through the jet, since the size of the drop varies with the nature of the oil.

McNaught's instrument for testing oils consists of two discs, the lower one provided with a raised edge and attached to a vertical spindle revolving in bearings; the upper one resting on a pivot. The space between the two discs having been filled with the oil to be tested, the lower disc is caused to revolve at a given speed. The upper disc is prevented from partaking of the motion of the lower disc, communicated through the oil, by a projecting pin which comes into contact with a pendulum; the extent to which the pendulum is removed from the per-

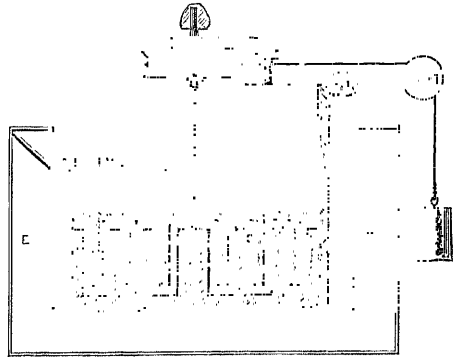


FIG. 30.—Section.

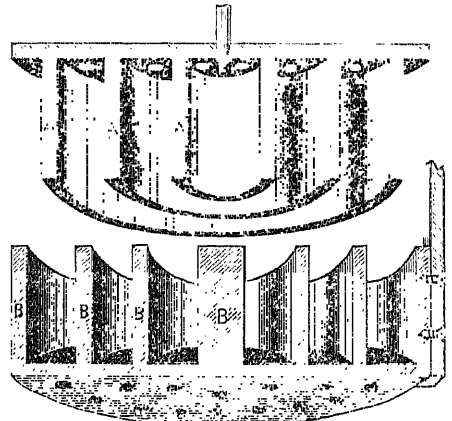


FIG. 31.—Perspective section.

A, A, A. Concentric rings,  $\frac{1}{16}$  in. thick,  $\frac{3}{4}$  in. deep. B, B, B. Ditto. C, C. Spaces of  $\frac{1}{16}$  in. between fixed and moving rings. D. Support for driving gear. E, E. Jacket.

pendicular being the measure of the viscosity of the oil.

The paddle viscometers of Napier of Glasgow and Cockerell of Manchester are based upon the principle of taking the speed of a paddle-wheel revolving in the oil as a measure of the viscosity. A series of concentric rings, on a vertical axis, revolving in concentric annular spaces (Figs. 30 and 31), and a hollow vertical drum revolving in a cylinder of slightly greater diameter containing the oil have also been employed by Napier. The use of a paddle-wheel for measuring the oil has besides the usual method of estimating viscosity suggested is to note the length of time occupied

in the ascent of a bubble of air through a given column of liquid, and Mills has carried out this idea by using hollow glass bulbs, but without obtaining promising results.

*g. Lubricating property by direct mechanical tests.* Machines have been devised by Thurston, Woodbury, Ingram and Stapfer, and others, for the mechanical testing of lubricating value. These machines are provided with accurately fitting frictional surfaces, between which the oil to be tested is placed, the heat and resistance at given speeds being determined. It cannot be said, however, that results of much practical utility in determining the value of lubricating oils have thus been obtained. Experience has, in fact, demonstrated that in any machine for the mechanical testing of such oils, the conditions under which the lubricants are to be actually employed must be reproduced. The writer has, therefore, been led to the conclusion that the viscosity of a mineral lubricant affords the best guide to its value.

the consumer being thus enabled to select from time to time oils similar to those which he has found by practical experience to afford the best results in the particular circumstances of his case. This branch of the subject has been treated in some detail in a paper by the writer published in the *Journal of the Society of Chemical Industry* (1886, 5, 121).

*h. Purity.* In the examination of mineral lubricating oils it is sometimes necessary to apply chemical tests. Oils intended for the lubrication of steam-engine cylinders should be pure hydrocarbons, saponifiable oils being liable to decomposition by the high-pressure steam, and the liberated fatty acids forming metallic soaps. The percentage of saponifiable oils present may be readily determined by treatment with alcoholic potash and extraction of the soap from the aqueous solution with ether. When a mineral lubricating oil is boiled with water and the liquids allowed to separate, the water should retain its transparency, and should exhibit no acid or alkaline reaction. Occasionally mineral lubricating oils are adulterated with resin oil, and this is increased by the addition of aluminium palmitate or oleate, or of india-rubber. If the presence of any of these adulterants is suspected the oil should be subjected to analytical examination.

### 6. Paraffin.

*a. Melting-point.* The so-called melting-point of paraffin is understood in the trade to be the temperature at which the melted material begins to solidify. The two methods chiefly adopted in determining this point are known respectively as the English test and the American test. The English test is conducted by melting the paraffin in a test-tube about  $\frac{3}{4}$  in. in diameter, and stirring the fluid material with a thermometer while the tube is held in the air until in the middle of the tube a point is reached at which the hydrocarbons liberates enough heat to arrest the reduction of temperature, and the mercury remains stationary for a short time. Saybolt has devised a convenient form of apparatus for applying this test simultaneously to several samples, the melted material being contained in a series of parallel troughs mounted on a carriage so as to travel backwards and forwards,

the thermometers being held rigidly above the troughs in a frame in such a position that the bulbs are just immersed. The American test is made by melting enough of the material to three-parts fill a hemispherical dish about  $3\frac{3}{4}$  ins. in diameter, allowing the paraffin to cool in the air and noting the temperature at which a very thin film extends from the sides of the vessel to a thermometer with a round bulb half an inch in diameter suspended in the middle of the dish so that the bulb is only three-fourths immersed. The melting-point by the American test is usually from  $21^{\circ}$ – $3^{\circ}$ F. higher than that indicated by the English test. Some operators prefer to note the temperature at which a minute quantity of the sample, previously fused into a tube, becomes solidified when the tube is allowed to cool slowly by the side of a sensitive thermometer in a beaker of water.

*b. Percentage of oil.* The determination of the percentage of oil in paraffin scale is a purely arbitrary test, as there is no natural line of demarcation between the solid and liquid hydrocarbons of petroleum. The test is made by subjecting the material to pressure and noting the loss in weight, but the results obtained depend upon the temperature at which the operation is conducted, the quantity of material in relation to the diameter of the press-cake and the amount and duration of pressure. The writer had some years ago a press (Fig. 32) con-

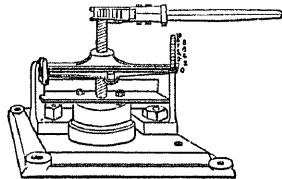


FIG. 32.

structed for the purpose with a steel crosshead, the deflection of which was magnified by levers, and the amount of pressure applied was thus indicated, and he now makes use of a press (Fig. 33) wherein a heavily weighted lever is used to regulate the pressure. Both these presses are provided with circular press-cups and plungers  $5\frac{1}{2}$  ins. in diameter, and the pressure employed in testing American paraffin scale is 9 tons on the total surface. The quantity of material operated upon is 500 grains, and the pressure is applied for 5 minutes at a temperature of  $60^{\circ}$ F. The paraffin is placed between circular pieces of calico cut with a steel punch to fit the press-cup, and the oil expressed is absorbed by a sufficient number of discs of blotting-paper placed above and below the cloth containing the cake. The temperature of the press-cup and the plunger is indicated by thermometers inserted in mercury-cups, and the paraffin is also brought to the standard temperature before being pressed. The testing press designed by McCutcheon (Figs. 34 and 35) is furnished with a helical steel spring, the extent of compression of which indicates the amount of pressure applied. Messrs. Clarkson and Beckett, of Glasgow, have made an excellent hydraulic press (Fig. 36) for the

purpose, which occupies less space than a lever press.

c. *Percentage of water and dirt.* The percentage of water in paraffin scale may be

determined by heating a weighed quantity in an evaporating dish to a temperature somewhat above the boiling-point of water, the melted paraffin being continuously stirred until the

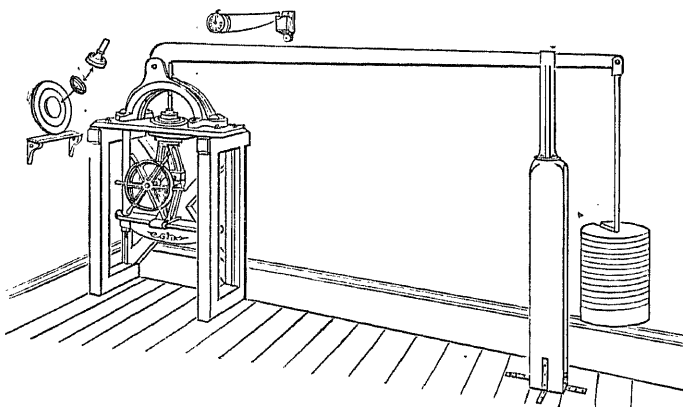


Fig. 33.

whole of the water has been driven off, when the loss in weight is noted. If the quantity of water present is large the percentage may be determined

charge of 50 grams of paraffin) the lower part of which is graduated. In the use of this instrument the greater portion of the melted paraffin may be readily poured off by removing the tube from the heating-bath when the water has separated, and plunging the lower end into cold water so as to seal the water by causing the solidification of a layer of paraffin above it.

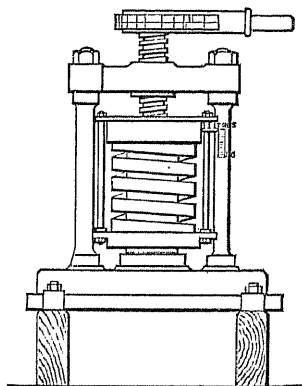


Fig. 34.

by distillation or by subsidence, the paraffin being retained in a melted state until the water

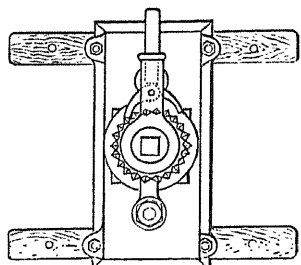


Fig. 35.

latter test, consisting of a bulbous tube (taking a

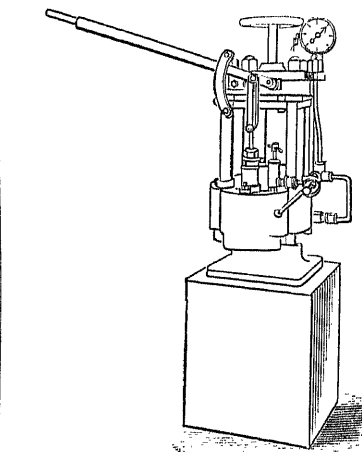


Fig. 36.

completed by dis- warm petroleum method of testing, the dirt is usually estimated with the water, but if the proportion of dirt is considerable it should be collected on a filter paper, washed with mineral spirit, dried and weighed.

The following methods of testing Scotch paraffin scale and heavy mineral oils were agreed upon by the chief chemists of the Scottish Mineral Oil Association, Price's Patent Candle Company, and the writer.



## I. SCALE ANALYSIS.

1. *Sampling of hard scale.* The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, waggon, or bin.

2. *Preservation of samples of scale.* Immediately after the sample has been drawn it is mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

3. *Determination of oil in scale.* (a) *Press to be used.* While no one special form of press is recommended for general adoption, the press used must be capable of indicating the pressure which the scale is placed under, and of pressure to have an effect on the scale.

(b) *Preparation of the sample.* A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool over night to a temperature of 60°F. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(c) *Quantity of scale to be used.* The quantity of scale to be used in the determination of oil is to be 250 grains, which quantity may, however, be reduced to 150 grains in the event of the scale containing much oil (over 7 p.c.). With 'soft' scale the smaller quantity should be taken.

(d) *Temperature at which the scale is to be pressed.* The temperature of the scale and the press is to be 60°F.

(e) *Time during which the scale is to remain under pressure.* The scale is to remain under pressure for 15 minutes.

(f) *Pressing cloths and papers.* Fine linen pressing cloths and a number of layers of filter-paper, sufficient to absorb all the oil, to be used. The exterior papers must not be soiled by oil.

(g) *Pressure to be applied.* The maximum pressure is to be 10 cwt. per square in. and the working pressure 9 cwt. per square in.

4. *Determination of water in scale.* The amount of water present in scale may be determined by either of the following processes:

(a) *Distillation from a copper flask.* From 1 to 2 lbs. of the scale are heated in a conical copper flask of about the dimensions shown in the annexed sketch; this is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp, the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with

hydrated gasoline or naphtha and added to the principal quantity.

(b) *Price's Company's method.* 500 grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 230°F. until bubbles cease to be given off; the loss is then determined.

500 grains of the same scale, which has been freed from its water and dirt by melting at a

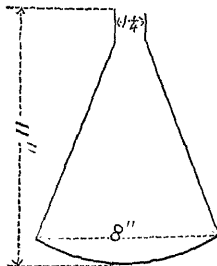


Fig. 37.

gentle heat and subsidence, are to be heated in the same way, to a similar temperature, and for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment, and the remainder is then to be taken as the quantity of water present.

5. *Determination of dirt in scale.* The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried and weighed. When available, the quantity of scale to be used in the determination of the percentage of dirt should not be less than 7000 grains.

6. *Calculation of the results of the analysis of scale.* As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

7. *Determination of the melting (setting) point of solid paraffin.* This is to be determined by what is known as the 'English' test, i.e. a test-tube about 1 in. in diameter is filled to the depth of about 2 ins. with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

## II. FLASHING-POINT OF HEAVY MINERAL OIL.

8. *Determination of the flashing-point of heavy mineral oil.* The oil cup and cover of the ordinary 'Abel' flash-point apparatus are to be employed. The cup is filled with oil in the usual manner, and the rate of heating is to be such that at least 15 minutes are taken in raising the temperature of the oil to 300°F. In the event, however, of a dispute arising as to the correct flashing-point of a heavy mineral oil, the question is to be decided by means of the 'Pensky-Martens' apparatus (J. Soc. Chem. Ind. 8, 734).

### III. VISCOSITY OF MINERAL OIL.

9. *Determination of the viscosity of mineral oil.* The instrument known as the 'Redwood' viscometer is that which is to be employed in the determination of the viscosity of mineral oils. The instrument is to be standardised according to the method given by Mr. Boverton Redwood (J. Soc. Chem. Ind., 1905, 127). Ordinary results are to be expressed, as the time in seconds which 50 c.c. of the oil take to flow through the orifice at a temperature of 70°F.

### IV. SETTING-POINT OF MINERAL OIL.

10. *Determination of the setting-point of mineral oil.* This is determined in the following manner. Into a test-tube having a diameter of about 1½ ins. the oil to be tested is added to the depth of about 2 ins.; the tube is then immersed in a bath of ice and water, the oil being slowly stirred. The bath is cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil until two experiments give concordant results, the temperature so found being the setting-point.

### 7. Gas and fuel oils.

'Gas oils' (mineral oil distillates used in the manufacture of gas for illuminating purposes or for the enrichment of coal-gas) are tested for specific gravity, flash-point, and freedom from water and dirt. In some cases a distillation test designed to secure uniformity in the oils supplied is also carried out.

Oils intended for use as liquid fuel are examined for the presence of water and of solid particles of foreign matter capable of blocking the burners, as well as for specific gravity, flash-point, fluidity at 32°F., calorific value, and percentage of sulphur.

*Calorific value.* This is best determined by burning one gram in a bomb calorimeter of the Mahler or similar type. Accuracy to within about half of 1 p.c. may be obtained with careful working.<sup>1</sup>

*Sulphur.* After the determination of the calorific value, the gaseous products of combustion in the bomb are led through a slightly alkaline scrubber, the liquid in which is added to the rinsings of the bomb and the whole precipitated with barium chloride in the usual manner.

B. R.

**PE-TUN-TSE, PE-TUN-SE, or PETUNTZITE**  
v. CHINA-STONE.

**PEUCEDANUM (ANETHUM) GRAVEOLENS** (Benth. et Hook.). The common Dill, cultivated in England and the South of Europe. Has a hot sweetish taste; is used in medicine and in the preparation of spirituous cordials.

**PEWTLER**

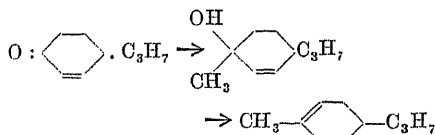
**PHASEOLUNATIN** v. GLUCOSIDES.

**PHELLANDRENE** C<sub>10</sub>H<sub>16</sub> is a terpene which occurs in many oils such as that of *Eucalyptus amygdalina* (Labill.) (Baker and Smith, J. Soc.

Chem. Ind. 1899, 302; Wallach, Annalen, 1905, 343, 28); in cinnamon oil (Dayk, Chem. Zentr. 1896, ii. 358; Schimmel & Co., *ibid.* 1910, i. 1720); in the oils of schinus molle (Wallach, *ibid.* 1905, ii. 674); of *Juniperus phoenicea* (Linn.) (Rodie, Bull. Soc. chim. 1906, [iii.] 35, 922); of *Abies sibirica* (Ledeb.) (Schindelmeiser, Chem. Zeit. 1907, 31, 759); of the sassafras bark and leaves (Power and Klebber, Chem. Zentr. 1897, ii. 42); in the seeds of *Myristicifera* (Schindelmeiser, *ibid.* 1907, i. 1794); in the resins of elemi wood (*Canarium luzonicum* [Miq.]) (Wallach and Rheindorf, Annalen, 1892, 271, 310; Bacon, Chem. Zentr. 1909, ii. 1448); in bitter fennel oil (Cahours, Annalen, 1842, 41, 74; Wallach, *ibid.* 1887, 239, 40; *ibid.* 1904, 336, 10); in water fennel oil (*Oenanthe Phellandrium* (Lam.)) from which the name is derived (Pesci, Gazz. chim. ital. 1886, 16, 225), and in many other oils (see Biochemisches Handlexikon, 1910, vii. 295).

It is one of the most unstable of the terpenes, and occurs in two modifications, the  $\alpha$ - and  $\beta$ - or *pseudo*, the former of which is usually present in greater quantity than the latter. Neither of these has, however, ever been obtained quite pure (Kondakoff, J. pr. Chem. 1908, [ii.] 78, 42).

$\alpha$ -Phellandrene exists in dextro- and lævo-rotatory modifications. The chief sources of  $\alpha$ -phellandrene are bitter fennel, elemi, and schinus oil. It is also the chief constituent in the dry distillation of certain elemi resins, whilst the chief source of  $\beta$ -phellandrene is eucalyptus oil (Wallach, Annalen, 1904, 336, 10). The purest natural  $\alpha$ -phellandrene so far obtained has b.p. 61°/11 mm., sp.gr. 0.844 at 19° ( $\beta$ - $\alpha$ ), and b.p. 65°/12 mm., sp.gr. 0.846, at 19° ( $\beta$ - $\alpha$ ), at ordinary pressure the b.p. is 173°-176°. The source of the  $\beta$ -phellandrene has been synthesised from isopropyl- $\Delta^2$ -hexenone by treating the latter with magnesium methyl iodide thus:



(Wallach, Annalen, 1908, 359, 265; *ibid.* 362, 281). It has b.p. 175°-176° (decomp.), sp.gr. 0.841 at 22°.

$\alpha$ -Phellandrene has also been synthesised from  $\Delta^6$ -menthene-2-one by treating it with phosphorus pentachloride and reducing the product thus obtained with zinc-dust in methyl alcohol solution, or by reducing menthenone-2-oxime with zinc-dust and glacial acetic acid, and distilling the  $\Delta^6$ -menthencamine so formed *in vacuo* with phosphoric acid. The  $\alpha$ -phellandrene so obtained has b.p. 66°/14 mm., 70°/15 mm., sp.gr. 0.8473 at 21°  $d_{20}^{20} + 45^\circ$  (Harries and Johnson, Ber. 1905, 38, 1832; see also Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193; 1907, [ii.] 75, 141).

$\alpha$ -Phellandrene combines directly with two atoms of bromine forming a dibromide which, when boiled with alcoholic potash, yields cymene (Wallach and Herbig, Annalen, 1895, 287, 371; Bacon, *l.c.*). When treated with alcoholic

<sup>1</sup> A full translation into English of the descriptive pamphlet issued by the makers of the Mahler bomb is included in Ilick's Mineral Oil Testing (Griffin).

sulphuric acid  $\alpha$ -phellandrene yields terpinene (Wallach, Annalen, 1887, 239, 44; 1889, 252, 102); and when reduced with sodium and amyl alcohol it yields  $\Delta^1$ - $\gamma$ -menthene  $C_{10}H_{18}$ , b.p. 122° (sp. gr. 0.829 (Semmler, Ber. 1903, 36, 1035, 1753; Bacon, l.c.). On oxidation with potassium permanganate  $\alpha$ -hydroxy- $\beta$ -isopropylglutaric acid  $C_8H_{14}O_5$  and its lactone  $C_8H_{12}O_4$  are formed; but when it is exposed to atmospheric oxygen *dihydroxyphellandrene*  $C_{10}H_{18}O_2$  is produced. The latter crystallises in needles, m.p. 164°-165° (Clover, Amer. Chem. J. 39, 613).

Phellandrene reacts with halogen acids forming mono- and di-additive compounds. *Phellandrene monohydrochloride* has b.p. 80°-83°/1 mm., and when boiled with excess of alcoholic potash yields *dipentene* (Bacon, l.c.; see also Wallach, Annalen, 1887, 239, 44; Chem. Zentr. 1902, i. 1293; Kondakoff and Schindelmeyer, l.c.; Kondakoff, *ibid.* 1908, 78, 42). The most characteristic compounds of phellandrene are the nitrites or nitrosites  $C_{10}H_{16}NO\cdot NO_2$ . They were first discovered by Cahours, and are prepared by the action of nitrogen oxides on the corresponding phellandrene in ligroin solution or by mixing an equal weight of aqueous sodium nitrite with a solution of the phellandrene in light petroleum and then adding gradually the equivalent quantity of glacial acetic acid. They are purified by solution in acetone and fractional precipitation with water or by dissolving in chloroform and precipitating with methyl alcohol (Cahours, l.c.; Wallach and Herbig, Annalen, 1895, 287, 373; Wallach, *ibid.* 1900, 313, 345; 1904, 336, 13; Helbronner, Compt. rend. 1901, 133, 43; Schindelmeyer, Chem. Zeit. 1907, 31, 759).

$\alpha$ -Phellandrene yields two modifications which may be regarded as *cis*- and *trans*-forms:

*trans*-Modification has m.p. 113°-114° (Wallach, 120, l.c.; Chem. Zentr. 1901, ii. 544), but according to Clover (l.c.) the melting-point depends on the temperature of crystallisation of the nitrosite (see also Leimbach, l.c.)  $[\alpha]_D +136^\circ$ - $143^\circ$  (from *l*-phellandrene),  $[\alpha]_D -138^\circ$  (from *d*-phellandrene).

*$\beta$ -Modification*, m.p. 105°-106°  $[\alpha]_D -40.8^\circ$  (from *l*-phellandrene),  $[\alpha]_D +45.8^\circ$  (from *d*-phellandrene).

The nitrosites do not react with bromine, and are not readily attacked by potassium permanganate, the products of oxidation being active isopropylsuccinic acid, and isobutyric acid. When oxidised with nitric acid, the products are trinitrotetrahydrocymene (chiefly)  $C_{10}H_{15}N_3O_8$ , m.p. 130°-137°, terephthalic, isobutyric and isopropylsuccinic acids. When reduced with zinc-dust and glacial acetic acid, the nitrosites yield  *$\alpha$ -phellandrene diamine*  $C_{10}H_{16}(NH_2)_2$ , b.p. 251°-254°, 132°-134°/17 mm. (Wallach, Annalen, 1902, 324, 270; *ibid.* 1904, 336, 42; Kondakoff, J. pr. Chem. 1903, [ii.] 68, 294), but when reduced with sodium and alcohol, they yield tetrahydrocarveol, and tetrahydrocarvylamine. The action of hydrochloric acid and of sulphuric acid and of ammonia on the nitrosites has also been studied (Wallach, Annalen, 1904, 336, 28, 28; *ibid.* 1900, 313, 346).

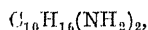
*Nitro- $\beta$ -phellandrene* is obtained by the action of nitric acid or acetyl chloride on the nitrosite (Annalen, 1887, 239, 42; 1895, 287, 374; 1904, 336, 31; 1900, 313, 349; Semmler, Ber. 1903, 36, 1754). It is a pale yellow oil with a quinone-like odour, b.p. 134°-138°, 125°-129°/9 mm., and gives with sodium and alcohol the same reduction products as the nitrosite. Its optical rotation is in the same sense as that of the nitrosite employed.

*$\beta$ - or pseudo-Phellandrene* is obtained chiefly from water-fennel oil, also from schinus oil, and in small quantities from *Thymus* and *Origanum*. Attempts have been made to prepare it artificially by treating carvomenthenedibromide with alcoholic potash (Kondakoff and Schindelmeyer, J. pr. Chem. 1905, [ii.] 72, 193), or by treating isopropylhexenone with bromacetic ester in presence of zinc; then removing water from the hydroxy ester so formed, and hydrolysing the product (Wallach, Chem. Zentr. 1908, i. 2166). The substances so obtained gave the reaction of  $\beta$ -phellandrene, but could not be obtained pure. It has b.p. 170°-172°, 57°/11 mm., sp. gr. 0.8520 at 20°,  $[\alpha]_D +18.54$ . On reduction it yields the same products as phellandrene as the  $\alpha$ -compound, and it combines with two atoms of bromine, forming a dibromide which, unlike the  $\alpha$ -dibromide, reacts with alcoholic potash forming *isopropyl- $\Delta^2$ -cyclohexene-4-one*, b.p. 125°-135°/10 mm. (Wallach, *ibid.* 1905, 340, 1; Semmler, Ber. 1903, 36, 1753).  $\beta$ -Phellandrene reacts with hydrochloric acid, forming pinene (Wallach, *ibid.* 1905, 340, 1; J. pr. Chem. 1907, [ii.] 75, 141).

When  $\beta$ -phellandrene is oxidised with excess of potassium permanganate, the final product is isobutyric acid, but at a low temperature and with excess of potassium permanganate the following products are formed: isopropyl- $\Delta^2$ -cyclohexene-4-one, and a *trans*-isomer of isobutyric acid, b.p. 150°/10 mm., which is identical with steam-volatile isobutyric acid in steam (Wallach, Annalen, 1905, 340, 1; see also Semmler, Ber. 1903, 36, 1749). When oxidised with free oxygen,  $\beta$ -phellandrene yields 1-isopropyl- $\Delta^2$ -cyclohexene-4-one, b.p. 103°-106°/15 mm., sp. gr. 0.9387 at 26°, the semi-carbazone of which melts at 183°-184° (Wallach, Annalen, 1905, 343, 30).

*$\beta$ -Phellandrene nitrite or nitrosite*  $C_{10}H_{16}N_2O_3$  exists in two modifications;  *$\alpha$ -nitrosite* has m.p. 102°  $[\alpha]_D -159.3^\circ$ ;  *$\beta$ -modification* has m.p. 97°-98°, and is almost optically inactive (Wallach, Annalen, 1904, 336, 43; 1905, 340, 1).

The nitrites of  $\beta$ -phellandrene are more readily soluble than those of  $\alpha$ -phellandrene. On reduction with sodium and alcohol various basic products and cuminaldehyde (m.p. of semi-carbazone, 210°-211°) are formed, whilst if carefully reduced with zinc-dust and acetic acid *laevo-rotatory  $\beta$ -phellandrene diamine*



b.p. 260° (decomp.), 133°-135°/11 mm. is formed (Wallach, Annalen, 1902, 324, 278). This diamine gives a number of distinctive derivatives.

*Nitro- $\beta$ -phellandrene*  $C_{10}H_{16}NO_2$  is obtained by treating the  $\beta$ -nitrosite with ammonia or potash (Pisci, l.c.; Wallach, Annalen, 1904,

336, 44; 1905, 340, 3; *ibid.* 343, 38); on reduction it forms tetrahydrocuminyl and other basic substances. According to Baer (l.c.), in addition to the  $\alpha$ - and  $\beta$ -phenylacetic acids contained in elemi wood resins, there is another phellandrene having b.p. 175°-178°, sp.gr. 0.8375, at 30°/4° [ $\alpha$ ]<sub>D</sub><sup>20</sup> 82.4.

*Phellandral* (tetrahydrocuminylaldehyde) (v. *supra*)  $C_{10}H_{16}O$  has been obtained from *Phellandrium* by removal of the phellandrene. It boils with citral, and boils at 220°-230°, 89°/5 mm., sp.gr. 0.9445 at 15°,  $\alpha_D$  -36° 30'. It gives a semi-carbazone, m.p. 204°, an oxime, m.p. 87°-88°, and a phenylhydrazone, m.p. 122°-123°. On exposure to the air, it forms the crystalline acid  $C_{10}H_{16}O_2$ , and when oxidised with potassium permanganate it yields the dibasic acid  $C_8H_{10}O_4$  (J. Soc. Chem. Ind. 1904, 1236).

### PHENACETIN

$C_{10}H_{11}NO_2$  is prepared by ethylating *p*-nitrophenol by Kolbe's method (J. pr. Chem. [ii.] 27, 424), reducing the nitrophenetole and acetylating the resulting aminophenetole by boiling with glacial acetic acid (Platt, J. Anal. and Appl. Ch. 1893, 77; Hinsberg, *Annalen*, 1899, 305, 278; Täuber, D. R. P. 85988).

According to Paul (Zeitsch. angew. Chem. 1896, 587) phenacetin is prepared by heating a mixture of 16.7 grams of *p*-aminophenetole hydrochloride, 8.7 grams of sodium hydroxide, 83 grams of acetic acid under a reflux condenser for 3 hours. The mixture is then poured into ten times its volume of boiling water and the solution is filtered. On cooling, phenacetin separates out, and can be purified by repeated recrystallisations. The yield is 90 p.c. of the theoretical.

It crystallises in colourless needles, melts at 135°, and is sparingly soluble in water, soluble in glycerol, and readily soluble in alcohol or acetic acid (Hinsberg and Kast, *Chem. Zentr.* 1887, 358; Utescher, J. Soc. Chem. Ind. 1888, 87; Seidell, *Amer. Chem. J.* 1907, 1088). According to Dujardin-Beaumetz (*Chem. and Drug.* 33, 244), phenacetin, if toxic, is only so in slight degree. It is a safe and trustworthy antipyretic, entirely free from injurious secondary effects, and in doses of 0.2-0.5 gram produces a gradual lowering of temperature during 4-6 hours, when a maximum depression of 2° is reached, D.-B.; H. and K.; U.; Ghillany, J. Soc. Chem. Ind. 1887, 676; Kobler, *Chem. Zentr.* 1887, 1092; Hoppe, *ibid.* 1888, 609; Rumpf, *ibid.* 1888, 1103. In larger doses (1-2 grams) it acts as an anti-neuralgic.

Pure phenacetin should answer to the following tests (Platt, l.c.):—

(1) When boiled with hydrochloric acid, the filtrate of the cold diluted solution produces a ruby-red colour on the addition of 2 or 3 drops of potassium dichromate.

(2) After boiling with water, the cooled filtered solution should remain clear on the addition of bromine water.

(3) Boiled with hydrochloric acid and ferric chloride, a red colour is produced.

(4) Boiled with caustic potash, alcohol is produced.

(5) Heated with alcohol and sulphuric acid, ethyl acetate is produced.

(6) Sodium persulphate produces a yellow colour when warmed with phenacetin, and this deepens to orange on boiling.

(7) Bromine water when heated with phenacetin solution gives a rose-colour.

(8) With Millon's reagent phenacetin gives a yellow colour passing to red, nitrous fumes are also given off and a yellow precipitate separates (Barral, J. Pharm. Chim. 1904, 237).

(9) When boiled with phosphoric acid of sp.gr. 1.7 a rose colour is produced, passing through red, violet-bluish-green to a dirty green (Raikow and Schtarbanow, *Chem. Zentr.* 1900, i. 999).

Phenacetin may contain as impurities or adulterations, acetanilide, antipyrine, quinine, exalgin, and other substances (Mannich, B. Pharm. 1906, 57). It also occurs as an impurity in antipyrine and other pharmaceutical substances. Acetanilide may be distinguished by the following methods.

0.1 gram of the sample is boiled with 3 c.c. of a 50 p.c. sodium hydroxide solution, then cooled and shaken with 5 c.c. of sodium hypochlorite solution. If acetanilide be present a purple- or brownish-red turbidity is produced, but if the sample be pure, a clear yellow liquid is obtained (Beringer, *Chem. and Drug.* 1903, 377).

0.5 gram is boiled with 6 c.c. of water, cooled, filtered, and the filtrate boiled with dilute nitric acid and potassium nitrite. Then a drop or two of Plugge's phenol test is added, and the solution boiled. The appearance of a red colour indicates acetanilide; 2 p.c. of the latter can thus be detected (Schroeder, *Arch. Pharm.* [iii.] 27, 226). 0.5 p.c. acetanilide can be detected by boiling a gram of the sample with 15 c.c. of water, the solution is then cooled and filtered. On addition of bromine water, a turbidity is produced if the impurity is present owing to the separation of *p*-bromacetanilide (Guasti, L'Orosi, 17, 111).

To detect phenacetin, exalgin, and acetanilide in a mixture, 1 gram of the mixture is treated with 2 c.c. chloroform, which dissolves the exalgin. In aqueous solution antifebrin gives with bromine water a crystalline bromine compound, whereas the other two substances do not give this (Hirschsohn, *Pharm. J.* 20, 710). Or 2-4 c.c. of the solution is boiled with potash in a test-tube fitted with a rubber cork and bent tube leading into a tube containing 1-3 c.c. of bleaching powder. If acetanilide is present the first few drops produce a violet colour. Exalgin gives a green, turning to a greyish-green colour; if antipyrine is present a yellowish-green colour is produced, whilst if none of these impurities is present, at first the solution remains colourless, then a vermillion-red turbidity is produced, and finally a red substance separates on the surface of the liquid, which itself remains clear yellow (Raikow and Schtarbanow, l.c.).

The presence of quinine can be detected by the addition of chlorine water and ammonia when, if quinine is present, a light blue colour will be produced, whereas if the sample is pure the colour is violet-yellow (Sestini and Campani, L'Orosi, 14, 304); or the solution is agitated with bromine vapour and ammonia added drop by



after removal of acid and basic constituents, the residue is freed from fluorene and diphenylene oxide by fusion with caustic potash at 300°, followed by extraction with hot water. The residue is then distilled to obtain the pure hydrocarbon (Akt. Teer-u. Erd-Oel Ind. D. R.-P. 130679; Eng. Pat. 5047 of 1901; cf. Kraemer and Weissgerber, Ber. 1901, 34, 1665).

On the laboratory scale, phenanthrene is purified conveniently by conversion in alcoholic solution into the *picrate*, which crystallises in golden-yellow needles, m.p. 143°–145°, and on treatment with ammonia yields the pure hydrocarbon (Limpricht, Ber. 1873, 6, 532).

**Properties.**—Phenanthrene crystallises in colourless scales, m.p. 100°, b.p. 340°. It is insoluble in water, but readily soluble in hot alcohol, ether, carbon disulphide, acetic acid, or benzene, showing blue fluorescence in solution. 100 parts of toluene dissolve 33.02 parts at 16.5°; 100 parts of absolute alcohol dissolve 2.62 parts at 16°; or 10.08 parts at 78° (Beehi, Ber. 1879, 12, 1978); and 100 parts of 95 p.c. alcohol dissolve about 2 parts at 13°–14° (Gräbe, Annalen, 1873, 167, 136).

**Reactions.**—(1) Oxidising agents convert phenanthrene into *anthracene* and by further oxidation into *carbazone* and *carbazole*. Ostermayer, *loc. cit.*, but 100 p.c. sulphuric acid and some mercury at 300° *phthalic acid* is obtained (Bad. Anilin- u. Soda-Fab. D. R.-P. 91202; Eng. Pat. 18221 of 1906).

(2) Chlorination in presence of halogen carriers leads to the production of 9:10-dichloro-phenanthrene,  $\text{m.p. } 160^{\circ}\text{--}161^{\circ}$  (J. Schmidt and Ladn, *Ber. Bunsenges. Physik. Chem.*, 44(3), and of 2:9:10-trichloro-phenanthrene, needles,  $\text{m.p. } 123^{\circ}\text{--}124^{\circ}$  (Schmidt and Ladn, *ibid.* 1906, 39, 3892).

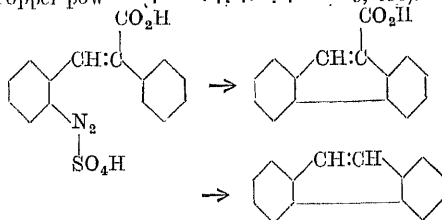
(3) With bromine in the cold it forms the *dibromide*, prisms, m.p. 98°, which, heated at its melting point, or with water, decomposes into *9,10-dibromophenanthrene*, prisms, m.p. 63° (Fittig and Ostermayer, *Annalen*, 1873, 166, 363; Hayduck, *Ze.*; Zetter, *Ber.* 1878, 11, 165; Austin, *Chem. Soc. Trans.* 1908, 93, 1763). Bromination in boiling chloroform solution leads to the formation of 3:9- (or 10:4)-*dibromophenanthrene*, needles, m.p. 146° (Schmidt and Lieber, *Ber.* 1904, 37, 3577) from phenanthrene, but of 2:7-*dibromophenanthrene*, needles, m.p. 199°–200°, from  $\alpha$ -tetrahydrophenanthrene (Schmidt and Metzger, *ibid.* 1907, 40, 4562).

(4) By nitric acid, it is converted into nitro derivatives like naphthalene and not oxidised to guirone like anthracene.

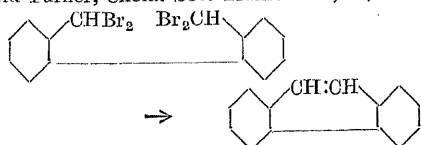
*Constitutions and syntheses.*—The structural formula assigned to phenanthrene at the head of this article was adopted originally to exhibit the relationship existing between the hydrocarbon and diphenic acid, its oxidation product (Fittig and Ostermayer, *loc. cit.*; Schultz, *Annalen*, 1879, 196, 1; 1880, 203, 95), or phthalic acid (*cf.* Anschütz and Japp, *Ber.* 1878, 11, 211). It has been confirmed by several syntheses, from among which three may be selected for reference as establishing the presence of specific radicles or linkings:—

(i.) Relationship to ethylene: Production

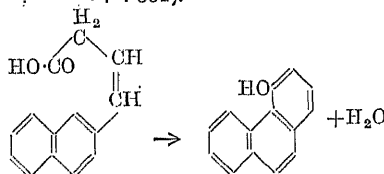
of phenanthrene by distilling phenanthrene-9-carboxylic acid obtained by the interaction of diazotised phenanthrene-9-carboxylic acid and copper powder (see, for example, [1, 2, 3, 4, 5, 6, 7, 8, 9, 496]).



(ii.) Relationship to diphenyl: Production of phenanthrene by debrominating  $\omega\omega'\omega'$ -tetrabromo-2 : 2'-ditolyl by means of sodium (Kenner and Turner, Chem. Soc. Trans. 1911, 99, 2112).



(iii). *β*-Naphthol to *α*-naphthalene: Production of *α*-naphthalene by heating *β*-naphthol, which is prepared from *β*-naphthol by the Perkin reaction (Ludewig, 1903, p. 351).<sup>1</sup>



Pschorr's method has proved to be of wide application in the synthesis of phenanthrene derivatives of known constitution from substituted benzene, benzoic acids, and, particularly, substituted phenols.

group of opium alkaloids to be elucidated.

Chemical activity in the phenanthrene molecule is manifested chiefly at the ethylenic double linking, shown between carbon atoms numbered 9 and 10 in the formula at the head of this article. Here the addition of hydrogen and bromine takes place, here oxidation leading to the production of phenanthraquinone occurs, and here disruption of the molecule follows when more powerful oxidising agents are used—as in the formation of diphenic acid. For the same reason (retaining orientation in the phenanthrene molecule, oxidation to diphenic acid is important, as—when substituents occur in positions other than 9 or 10 or 9 and 10—they are found in corresponding positions in the resulting diphenic acids.

Phenanthrene has little value in technical chemistry, but its relationship to some of the alkaloids of opium and of *Corydalis* is of much interest. These alkaloids are methoxy or hydroxy derivatives of tetra- or

1 Although phenanthrene can be synthesised from naphthalene, the reverse operation has not been accomplished, the lateral rings remaining intact until the middle ring has been broken down by oxidising agents.

<sup>1</sup> Zetter, also, has described two dibromophenanthrenes, but one of them—the  $\beta$ -compound—is now known to be  $\beta$ -dibromofluorene (Werner and Egger, Ber. 1904, 37, 3027).

parent substance complex in the case of the opium alkaloids being 3:6-dihydroxy-4:5-phenanthrylene oxide, in the molecule of which (a) rings I and II are hydrogenated in morphine and codeine, but only ring I in thebaine; (b) the hydroxyl radicle is methylated in ring I in codeine, but in both rings in thebaine. Of the *Corydalis* alkaloids bulbocapnine, corytuberine, and corydine less is known, but a relationship has been established between their structure, and that of apomorphine (Gadamer, Arch. Pharm. 1911, 249, 503; cf. Dobbie and Lauder, Chem. Soc. Trans. 1902, 81, 145).

The connection between the opium alkaloids and hydroxyphenanthrenes has led to the study of the physiological action of phenanthrene and its derivatives. Phenanthrene and its hydrogenated derivatives are harmless (Hildebrandt, Arch. exp. Path. Pharm. 1908, 59, 140), but 2-, 3-, or 9-hydroxyphenanthrene administered subcutaneously gives rise to acute tetanic convulsions, observed also with certain of the sulphonic acids (Bergell and others, J. physiol. Chem. 1903, 38, 16). There is no evidence to show that phenanthrene derivatives from the molecules of which a quinoline or isoquinoline ring is absent can exercise a narcotic action.

#### PHENANTHRENE HYDRIDES.

9:10-Dihydrophenanthrene is obtained when phenanthrene is reduced in boiling amyl alcohol solution by sodium, or in presence of finely-divided nickel at 200° by hydrogen (J. Schmidt and Mezger, Ber. 1907, 40, 4240), or in presence of nickel oxide by hydrogen at 320° under 100 atmos. (Ipatiew, Jakowiew and Rakitkin, Ber. 1908, 41, 999). It forms leaflets from alcohol, m.p. 94°-95°, b.p. 312°-314° under 739 mm., and does not react with bromine. The *picrole* forms scarlet needles, m.p. 135°-137° (J. Schmidt and Mezger, l.c.).

By further reduction with these agents  $\alpha$ - and  $\beta$ -tetrahydro-,<sup>1</sup> and hexahydro-, octahydro-, decahydro-, and  $\alpha$ -octahydro-phenanthrenes have been obtained.

The densities of which fall as the number of hydrogen atoms in the molecule is increased. The  $\alpha$ -tetrahydro derivative they do not form picrates (J. Schmidt and Mezger, l.c.).

#### PHENANTHRENESULPHONIC ACID.

Phenanthrene-2-sulphonic acid is effected by the action of sulphuric acid, of an equal weight of phenanthrene, Annalen, 1873, 227, 166; and Japp, Ber. 1877, 10, 1661; Japp, Trans. Chem. Soc. 1880, 37, 83; with two-thirds of this weight at 170°<sup>2</sup> (Morton and Geyer, J. Amer. Chem. Soc. 1880, 2, 203);

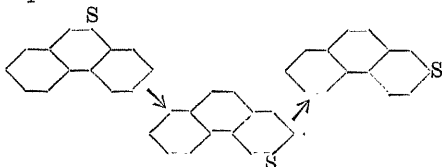
<sup>1</sup> These tetrahydrophenanthrenes are probably the 2:7:9:10- and 4:5:9:10- derivatives, but it is not known which of them has the former, and which the latter constitution.

<sup>2</sup> The " $\beta$ -acid" obtained in addition to Graebe's acid by these authors is not identical with Japp's  $\beta$ -acid, and appears to have been 3-acid mixed with some impurity, probably 2-acid (cf. Werner, l.c.).

with an equal weight of sulphuric acid at different temperatures between 80° and 165° (Werner, Annalen, 1902, 321, 257); and with chlorosulphonic acid (Pechorr, Ber. 1901, 34, 4004). Disulphonation has been found to occur when phenanthrene is treated with anhydrosulphuric acid, Ber. 1880, 13, 314).

Three monosulphonic acids have been shown to occur in the products obtained by the aid of sulphuric acid. The first of these was isolated by Graebe, and converted by Schultz and Japp into a carboxylic acid, oxidisable to phenanthraquinonecarboxylic acid; it is the [ $\alpha$ -] or 3-acid, as it yields 3-hydroxyphenanthrene on fusion with caustic potash. The second was isolated by Japp, and by him oxidised to phenanthraquinone: it is the [ $\beta$ -] or 9(10)-acid. The third is the 2-acid discovered by Werner and Rekner (Werner, l.c.), which gives 2-hydroxyphenanthrene on fusion with caustic potash. With chlorosulphonic acid the product is a mixture of the 2- and 3-sulphonic acids.

The conditions under which these acids are obtained by means of sulphuric acid is shown in the scheme, which allows a comparison to be made with the course of sulphonation in the naphthalene series:



Best yield at 95°-100°; not detected above 130°.	Best yield at 120°-180°; very little above 180°.	Good yield at 120°-130°.
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For the separation of the isomerides fractional crystallisation of the lead, barium, calcium, or potassium salts is employed, the solubility in water in each case increasing from the 9(10)- to the 2-acid (Werner, l.c.).

**Phenanthrene-2-sulphonic acid** has not been crystallised. The *lead* salt,  $\text{PbA}_2 \cdot 2\text{H}_2\text{O}$ , is crystalline; the *potassium* salt,  $\text{KA}$ , and *ammonium* salt,  $\text{NH}_4\text{A}$ , form leaflets; and the *methyl ester* scales, m.p. 96°-98°, which show blue fluorescence (Werner, l.c.; Pechorr, l.c.).

**Phenanthrene-3-sulphonic acid** forms scales,  $\text{HA} \cdot 2\text{H}_2\text{O}$ , m.p. 88°-89°,  $\text{HA} \cdot \text{H}_2\text{O}$  m.p. 120°-121°;  $\text{HA}$ , m.p. 175°-... Annalen, 1909, 369, 106). The *lead* salt,  $\text{PbA}_2 \cdot 3\text{H}_2\text{O}$ , crystalline granules; *copper* salt,  $\text{CuA}_2 \cdot 4\text{H}_2\text{O}$ , scales; *ferrous* salt,  $\text{FeA}_2 \cdot 5\text{H}_2\text{O}$ , and *zinc* salt,  $\text{ZnA}_2 \cdot 4\text{H}_2\text{O}$ , crystalline powders; *barium* salt,  $\text{BaA}_2 \cdot 3\text{H}_2\text{O}$ , scales; *calcium* salt,  $\text{CaA}_2 \cdot 2\text{H}_2\text{O}$ , crystalline granules; *magnesium* salt,  $\text{MgA}_2 \cdot 4\text{H}_2\text{O}$ , scales; *potassium* salt,  $\text{KA}$ , scales; *ammonium* salt,  $\text{NH}_4\text{A}$ , scales, have been described (Sandqvist, l.c.). The *sulphonyl chloride* crystallises in rhombic prisms, m.p. 110°-111°, also 114°; the *amide* in scales, m.p. 190°; the *methyl ester* in scales, m.p. 119°; and the *ethyl ester* in needles, m.p. 108°.

**Phenanthrene-9 (10)-sulphonic acid** forms needles; the *barium* salt,  $\text{BaA}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , needles; the *potassium* salt,  $\text{KA}$ , needles; the *sulphonyl chloride* needles, m.p. 125°-5°; and the *anilide* prisms, m.p. 165° (Werner, l.c.). For other salts, cf. Sandqvist, Annalen, 1912, 392, 76.

## NITROPHENANTHRENES.

Of the five nitrophenanthrenes the 1-isomeride has not yet been prepared (J. Schmidt and Heinle, Ber. 1911, 44, 1490).

Earlier work on the nitration of phenanthrene with a large excess of fuming nitric acid led to the isolation of three compounds, termed  $\alpha$ - (m.p. 73°–75°),  $\beta$ - (m.p. 126°–127°), and  $\gamma$ - (m.p. 170°–171°) nitrophenanthrenes (G. A. Schmidt, Ber. 1879, 12, 1153). It has been shown that of these compounds the  $\alpha$ - and  $\gamma$ - with 4- and 3-nitro- the  $\beta$ -compound is a nitro derivative not of phenanthrene, but of fluorene, which accompanies this hydrocarbon in coal-tar (J. Schmidt and Heinle, l.c.).

For the production of nitrophenanthrenes J. Schmidt has employed two methods. In one, nitration is effected by nitric acid (sp.gr. 1.45) in presence of a mixture of acetic acid and acetic anhydride, leading to the formation of the four isomerides. A summary of the properties and yields of these substances, as recorded by J. Schmidt and Heinle, is given in the table—

NO <sub>2</sub>	Yield (approx.)	Crystallisation from alcohol	M.p.	Picrate
2-	20 p.c.	pale yellow rosettes	99°	none
3- <sup>1</sup>	2 p.c.	deep yellow needles	170°–171°	none
4-	20 p.c.	reddish yellow needles	80°–82°	none
9-	60 p.c.	orange yellow needles	116°–117°	98°–99°

In the second method use is made of one of the two additive compounds which phenanthrene, dissolved in benzene, forms with the nitrous gas obtained by the interaction of nitric acid and arsenious oxide. This substance, nitrodihydrophenanthrene oxide (m.p. 154°–155°), is converted by sodium methoxide into 9-nitrophenanthrene (J. Schmidt, Ber. 1910, 33, 3257):

$$\text{C}_6\text{H}_4\cdot\text{CH}=\text{O}-\text{CH}\cdot\text{C}_6\text{H}_4 \rightarrow 2 \text{C}_6\text{H}_4\cdot\text{CH}=\text{O} + \text{H}_2\text{O}$$

$\text{C}_6\text{H}_4\cdot\text{CH}(\text{NO}_2)(\text{NO}_2)\text{CH}\cdot\text{C}_6\text{H}_4 \rightarrow 2 \text{C}_6\text{H}_4\cdot\text{C}(\text{NO}_2)=\text{O}$  derivative, 9-

a yellow crystalline compound, decomposing at 100°, is obtained on mixing phenanthrene in dry powder with the liquefied nitrous gas (J. Schmidt, D. R.-P. 129990 of 1901).

## AMINOPHENANTHRENES.

Four aminophenanthrenes (phenanthrylamines) are known corresponding in orientation with the nitro-phenanthrenes. Three methods have been employed for their preparation:—

(i.) Reduction of the nitro compound by alcoholic ammonium sulphide (G. A. Schmidt, Ber. 1879, 12, 1156), or stannous chloride and hydrochloric acid (J. Schmidt and Strobel, *ibid.* 1901, 34, 1464), or zinc dust and alcoholic ammonia (J. Schmidt and Heinle, *ibid.* 1911, 44, 1498).

(ii.) Heating the hydroxy compound at temperatures above 200° with ammonia (Japp and Findlay, Chem. Soc. Trans. 1897, 71, 1123; J. Schmidt and Heinle, l.c.) is obtained in better yield with nitric acid of sp.gr. 1.56 (J. Schmidt and Heinle, l.c.).

Pschorr and Schröter, Ber. 1902, 35, 2728), or ammonio-calcium chloride, or—for the acetyl compound—ammonium chloride, sodium acetate, and acetic acid (Werner and Kunz, Ber. 1901, 34, 2525).

(iii.) Conversion of the carboxylic acid successively into the hydrazide, azide, and urethane, which is then heated with ammonia (Pschorr and Schröter, l.c.; Pschorr, Einbeck, and Spangenberg, Ber. 1907, 40, 2000).

The crystalline character and m.p. of each base and the m.p. of its acetyl and benzoyl derivatives are given in the table—

—	Base	Acetyl	Benzoyl
2-	crystals, 85°	225°–226°	—
3-a-	leaflets, 143°	{ 200°–201° <sup>β</sup>	213°–214° <sup>β</sup>
β-	leaflets, 87°5'		
4-	needles, 105°	190°	224°
9-a-	needles, 138°	{ 207°–208° <sup>a</sup>	190° <sup>a</sup>
β-	crystals, 104°		

As shown in the table, 3-aminophenanthrene (Werner and Kunz, l.c.; Werner, Annalen, 1902, 321, 312; cf. J. Schmidt and Sauer, Ber. 1911, 44, 3247) and 9-aminophenanthrene (J. Schmidt and Heinle, l.c.) exist in two forms—one stable, the other labile and convertible into it by being heated or kept for some time or acetylated. Both forms of each compound give the same acetyl or benzoyl derivative, from which by hydrolysis the stable form of the base (indicated by the Greek letter) is obtained. The nature of the isomerism has not been established, but it has been attributed to rearrangement of the linkings in the phenanthrene molecule in view of the fact that the two forms of the 9-isomeride have the same molecular weight (J. Schmidt and Heinle, l.c.).

Diazotisation of β-3-aminophenanthrene (J. Schmidt, Ber. 1901, 34, 3534; cf. Werner and Kunz, l.c.), and of 9-aminophenanthrene<sup>1</sup> (J. Schmidt and Strobel, Ber. 1903, 36, 2517) has been effected—in the latter case with the accompanying production of azoxy and azo

The oxime and dioxime of phenanthraquinone, on reduction with stannous chloride, yield 9-aminophenanthrene (Vahlen's morphine, Ber. 1902, 35, 3840 of 1902; B. 1902, 35, 3840 of 1902). 9-diaminophenanthrene respectively (Pschorr and Schröter, *ibid.* 3733). The former, when heated with water or dilute acid, is converted into 9-aminophenanthrene (Schmidt, D. R.-P. 141422 of 1902).

## HYDROXYPHENANTHRENES.

The hydroxy derivatives of phenanthrene (phenanthrols) have been investigated mainly as a consequence of the fact that phenanthrene has been established between the morphine and certain of the opium alkaloids. In many cases the hydroxy-

two forms of the 9-isomeride in (J. Schmidt and Heinle, l.c.), and there is no information as to both forms, or only the α-derivative can be diazotised.



phenanthrenes has been determined by Pschorr's synthetical method, which has shown itself to be of the first importance in the study of the degradation products of these alkaloids. In others, the constitution assigned depends on that of the sulphonic acids, from which some of

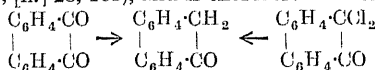
the hydroxy derivatives have been obtained by fusion with caustic alkali (*cf.* Werner, *Annalen*, 1902, 321, 276). The constitution, crystalline character, and melting-point of the hydroxy-phenanthrenes and of their ethers are given in the table:—

OH in	Hydroxyphenanthrenes and their ethers.	References.
1	Has not been isolated. <i>Methyl ether</i> , needles, m.p. 105°–106°; gives <i>picrate</i> , needles, m.p. 153°.	Pschorr, Wolfes and Buckow (Ber. 1900, 33, 162).
2	Forms scales, m.p. 169°; couples with diazotised bases; gives <i>acetate</i> , needles, m.p. 142°–143°, and <i>benzoate</i> , leaflets, m.p. 139°–140°. <i>Methyl ether</i> , leaflets, m.p. 100°–101°; gives <i>picrate</i> , needles, m.p. 124°. <i>Ethyl ether</i> , leaflets, m.p. 112°.	Werner and Kunz (Ber. 1901, 34, 2524); Pschorr and Klein ( <i>ibid.</i> , 4005); Werner and Rehner (Annalen 1902, 321, 305); Henstock (Chem. Soc. Trans. 1906, 89, 1528).
3	Forms needles, m.p. 122°–123°; couples with diazotised bases; gives <i>picrate</i> , m.p. 150° <i>acetate</i> , plates, m.p. 115°–116°, and <i>benzoate</i> , needles, m.p. 119°. <i>Methyl ether</i> , plates, m.p. 63°; gives <i>picrate</i> , red needles, m.p. 124°–5°. <i>Ethyl ether</i> , m.p. 46°.	Pschorr, Wolfes and Buckow ( <i>l.c.</i> ); Pschorr and Sumuleanu (Ber. 1900, 33, 1821); Werner and Kunz ( <i>l.c.</i> ); Schmidt (Ber. 1901, 34, 3535); Pschorr ( <i>ibid.</i> 4006).
4	Crystalline, m.p. 106°–109°; gives <i>acetate</i> , leaflets, m.p. 58°–59°. <i>Methyl ether</i> , leaflets, m.p. 68°; gives <i>picrate</i> , red needles, m.p. 187°–188°.	Pschorr and Jaeckel (Ber. 1900, 33, 1820); Ludwig (Annalen, 1911, 370, 361).
9 (10)	Forms large needles, m.p. 152°–153°; couples with diazotised bases; gives <i>picrate</i> , red needles, m.p. 183° <i>acetate</i> , needles, m.p. 77° and <i>benzoate</i> , needles, m.p. 96°–97°. <i>Methyl ether</i> , needles, m.p. 96°–97°.	Japp and Findlay (Chem. Soc. Trans., 1897, 71, 1115); Werner and Frey (Annalen, 1902, 321, 298); Pschorr and Schröter (Ber. 1902, 35, 2728).
2:3	Has not been isolated. <i>Dimethyl ether</i> , leaflets, m.p. 131°; gives <i>picrate</i> , needles, 127°–128°.	Pschorr and Buckow (Ber. 1900, 33, 1820).
3:4	Morphol, forms long needles, m.p. 143°; gives <i>diacetate</i> , needles, m.p. 159°. 3-Methyl ether, m.p. 65°; gives <i>picrate</i> , red needles, m.p. 131°. 4-Methyl ether, oil; gives <i>acetate</i> , needles, m.p. 93°–94°. <i>Dimethyl ether</i> , leaflets, m.p. 44°; gives red <i>picrate</i> , m.p. 105°–106°, and <i>dibromide</i> , m.p. 123°.	Fischer and Vongerichten (Ber. 1886, 19, 793); Knorr ( <i>ibid.</i> 1892, 25, 1147; 1894, 27, 1148); Pschorr and Sumuleanu ( <i>ibid.</i> 1900, 33, 1819, 1823); Vongerichten ( <i>ibid.</i> 352, 1825); Knorr ( <i>ibid.</i> 1904, 37, 3497); Knorr ( <i>ibid.</i> 1904, 37, 3497).
9:10	Forms needles, m.p. 146°; gives <i>monoacetate</i> , needles, m.p. 168°–170°; <i>diacetate</i> , flat prisms, m.p. 202°, and <i>dibenzoyl ether</i> , m.p. 230°–231°.	Pschorr and Koch (Annalen, 1902, 35, 2736, 3124); Knesch (D. R.-P. 151981 of 1903).
3:4:5	Forms scales, m.p. 148°. <i>Trimethyl ether</i> , m.p. 90°; gives <i>picrate</i> , brown scales or needles, m.p. 167°.	Vongerichten (Ber. 1906, 39, 1720); Pschorr and Koch (Annalen, 1912, 391, 54).
3:4:6	Has not been isolated. 3-Methyl ether, oil; gives <i>diacetate</i> , m.p. 162°–163°. 3:6-Dimethyl ether (heptaol), m.p. 94°; gives <i>acetate</i> , m.p. 118°–120°. <i>Trimethyl ether</i> , oil; gives <i>picrate</i> , m.p. 109°–110°.	Freund (Ber. 1897, 30, 1389); Pschorr, <i>Se.</i> 1902, 35, 2736, 3124 ( <i>ibid.</i> 4411); Knorr ( <i>ibid.</i> 37, 3499); Knorr (Annalen, 1910, 370, 361).
3:4:8	Has not been isolated. 3:4:8-Triethyl ether, m.p. 155°–156°. 3:4:8-Triethyl ether, m.p. 182°–183°. 3:4:8-Triethyl ether, leaflets, m.p. 164°–165°; gives <i>acetate</i> , prisms, m.p. 96°–97°. <i>Trimethyl ether</i> , leaflets, m.p. 138°; gives <i>picrate</i> , red needles, m.p. 139°–140°. 3:4:8-Triethyl ether, m.p. 100°; gives <i>picrate</i> , needles, m.p. 147°–148°.	Pschorr and Koch (Annalen, 1902, 35, 2736, 3124); Knorr and Schneider (Ber. 1906, 39, 1420); Pschorr, Kuhtz and Roth ( <i>ibid.</i> 3137).
3:4:9 (or 10)	Has not been isolated. 3-Methyl ether; <i>diacetate</i> , needles, m.p. 202°–204°.	Knorr and Schneider (Ber. 1906, 39, 1420); Pschorr, Kuhtz and Roth ( <i>ibid.</i> 3137).
1:3:5:6	3:5:6-Trimethyl ether, no description given. <i>Tetramethyl ether</i> , needles, m.p. 108°–109° gives <i>picrate</i> , red needles, m.p. 147°–148°.	Pschorr and Rettberg ( <i>l.c.</i> ); Pschorr and Knoefler (Annalen, 1911, 382, 50).

Among these hydroxyphenanthrenes there are several, about which the constitution given

in the table needs to be supplemented to make clear their properties and relationships.

9- (or 10-) **Hydroxyphenanthrene**, also known as phenanthrone, affords an example of keto-enolic isomerism in the phenanthrene series. It can be obtained from phenanthraquinone by partial reduction with hydriodic acid (Japp and Knecht, *Chem. Soc. Trans.* 1893, 63, 770), or from phenanthrene-9-sulphonic acid by reduction with iron and acetic acid (Lachowicz, *J. pr. Chem.* 1883, [ii.] 28, 168), and is therefore a ketone



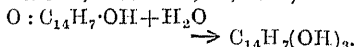
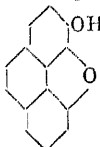
But its formation from phenanthrene-9-sulphonic acid by fusion with caustic alkali, its solubility in alkali, and its conversion into an *ortho*-azo compound (m.p. 165°) by Werner and Frey, *Annalen*, 1902, 321, 298, show it to be phenolic under other conditions.

#### *Hydroxyphenanthrenes from opium alkaloids.*

The degradation of opium alkaloids into nitrogen compounds containing relatively few carbon atoms and into derivatives of hydroxyphenanthrene free from nitrogen, has been accomplished by Hofmann's method of exhaustive methylation (Ber. 1881, 14, 494, 663), the products being decomposed by hydrogen chloride (Knorr, *ibid.* 1894, 27, 1147), acetic anhydride (Fischer and Vongerichten, *ibid.* 1886, 19, 792), heat (Schrötter and Vongerichten, *ibid.* 1882, 15, 1485), or hot caustic soda solution (Freund, *ibid.* 1897, 30, 1379). A list of decomposition products of this type is given by Knorr and Pschorr, Ber. 1905, 38, 3174. The following summary indicates the sources of the more important nitrogen-free degradation products of opium and *Corydalis* alkaloids.

**3:4-Dihydroxyphenanthrene** or **morphol** is formed when acetylmorphine methiodide and its 3-methyl ether when acetylcodeine methiodide are heated with acetic anhydride (Fischer and Vongerichten, Ber. 1886, 19, 792; Knorr, *ibid.* 1889, 22, 181, 1113; Vongerichten, *ibid.* 1896, 29, 65; 1897, 30, 2439), or morphenol methyl ether is reduced by sodium and alcohol (Vongerichten and Dittmer, *ibid.* 1906, 39, 1719). By the degradation of apomorphine the dimethyl ether of morphenol's carboxylic acid has been obtained, convertible into morphol dimethyl ether (Pschorr, Jaceckel and Fecht, Ber. 1902, 35, 4392; Pschorr, Einbeck and Spangenberg, *ibid.* 1907, 40, 1998).

**Morphenol** (3-hydroxy-4:5-phenanthrylene oxide) is the internal anhydride of 3:4:5-trihydroxyphenanthrene, into which it is converted by fusion with caustic alkali (Vongerichten and Dittmer, Ber. 1906, 39, 1718)



It is obtained from  $\beta$ -methylmorphimethine methiodide (Vongerichten, Ber. 1898, 31, 54; 1901, 34, 2722), or from morphenol's carboxylic acid by isolation of the acid (Vongerichten, *ibid.* 1900, 33, 35), or from morphenol's methyl ether by reduction with hydriodic acid (Vongerichten, *ibid.* 1901, 34, 3202). It forms no colouration in alcoholic chloride, dissolves in caustic soda, giving a yellow solution with blue fluores-

cence, and does not couple with diazotised bases. On reduction it yields *morphol* (Vongerichten, Ber. 1899, 32, 1522).

Its *methyl ether* forms needles, m.p. 65° (cf. Knorr, Ber. 1889, 22, 184; Vongerichten, *ibid.* 1898, 31, 54; 1900, 33, 358; Schryver and Lees, *Chem. Soc. Trans.* 1901, 79, 578); *acetate*, needles, m.p. 140°; and *benzoate*, needles, m.p. 123° (Vongerichten, *l.c.*).

**3:4:6-Trihydroxyphenanthrene** or **3-methyl ether** is obtained from codeine methiodide (Knorr, *ibid.* 1904, 37, 3501). The 3:6-dimethyl ether or *thebaol* results from boiling thebaïne with acetic anhydride (Freund, Ber. 1897, 30, 1386), and the trimethyl ether when the silver salt of the 8-carboxylic acid, obtained from morphothebaïne, is decomposed by heat (Pschorr and Rettberg, *Annalen*, 1910, 373, 65).

**3:4:8-Trihydroxyphenanthrene**. The 8-methyl ether is formed from  $\psi$ -iso-codeine methiodide (Knorr and Hoerlein, Ber. 1907, 40, 2039, 3350); and the trimethyl ether from the 5-carboxylic acid obtained from thebenine (Pschorr and Loewen, *Annalen*, 1910, 373, 71).

**3:4:9- (or 10-) Trihydroxyphenanthrene**. The *diacetate* of the 3-methyl ether is formed when thebaïne is heated with acetic anhydride (Knorr and Schneringer, *ibid.* 1907, 40, 2039, 3350; Pschorr, *ibid.* 1910, 373, 71).

#### *Vinylhydroxyphenanthrenes.*

As primary products of the Hofmann degradation of certain opium and *Corydalis* alkaloids, the following vinylmethoxyphenanthrenes have been obtained, which on oxidation yield the corresponding methoxyphenanthrenecarboxylic acids.

**5-Vinyl-3:4:8-trimethoxyphenanthrene**, from thebenine, forms *picrate*, red tablets, m.p. 110° (Pschorr and Massaciu, Ber. 1904, 37, 2789). The 8-ethoxy derivative forms plates, m.p. 78° (Pschorr and Loewen, *Annalen*, 1910, 373, 72).

**8-Vinyl-3:4-dimethoxyphenanthrene**, from apomorphine, forms rhombic prisms, m.p. 80°; *picrate*, violet needles, m.p. 128° (Pschorr, Jaceckel and Fecht, Ber. 1902, 35, 4391; cf. Pschorr, *ibid.* 1906, 39, 3124).

**8-Vinyl-3:4:6-trimethoxyphenanthrene**, from morphothebaïne, forms needles, m.p. 61°; *picrate*, reddish-violet needles, m.p. 125°-126° (Knorr and Pschorr, Ber. 1905, 38, 3157; Pschorr and Rettberg, *Annalen*, 1910, 373, 65).

**8-Vinyl-3:4-dimethoxy-5:6-methylenedioxyphenanthrene**, from bulbocapnine, forms yellow needles, m.p. 101° (Gadamer and Kuntze, *Arch. Pharm.* 1911, 249, 630).

#### PHENANTHRENECARBOXYLIC ACIDS.

The *carboxylic acids* have been prepared from the corresponding *anhydrides* obtained from the *anhydrides* or *ferrocyanide* (Schneringer, *ibid.* 1907, 40, 1661; Japp, *Chem. Soc. Trans.* 1880, 37, 83; Werner and Kunz, *Annalen*, 1902, 322, 323). Synthetically Pschorr has obtained the 3-carboxylic acid (1896, 29, 496), and the 8:9-dicarboxylic acid, the latter of which readily forms a well-crystallised anhydride (m.p. 233°-234°), and exhibits

the behaviour of a naphthalene *peri*-derivative (*ibid.* 1906, 39, 3107).

Phenanthrene-2-carboxylic acid, needles, m.p. 105°; forms acid on oxidation.

Phenanthrene-3-carboxylic acid ( $[\alpha]$ -acid), scales, m.p. 269°, forms the barium salt,  $\text{BaA}_2 \cdot 7\text{H}_2\text{O}$ , sparingly soluble needles; sodium salt,  $\text{NaA} \cdot 4\text{H}_2\text{O}$ , easily soluble scales; amide, scales, m.p. 227°–228°; nitrile, needles, m.p. 102°; and yields phenanthraquinone-3-carboxylic acid on oxidation.

Phenanthrene-9-(10)-carboxylic acid ( $[\beta]$ -acid), needles, m.p. 250°–252°, gives the barium salt  $\text{BaA}_2 \cdot 6\text{H}_2\text{O}$ , sparingly soluble tablets; sodium salt,  $\text{NaA} \cdot 5\text{H}_2\text{O}$ , easily soluble rhombic tablets; amide, needles, m.p. 226°; nitrile, needles, m.p. 103°; and yields phenanthraquinone on oxidation.

#### HYDROXYPHENANTHRENECARBOXYLIC ACIDS.

Hydroxyphenanthrenecarboxylic acids have been obtained (a) by oxidation of vinylhydroxyphenanthrenes; (b) from alkaloids by oxidation of vinylhydroxyphenanthrenes; (c) synthetically by Pschorr's method from substituted cinnamic acids. As will be seen from the following summary, in few cases only have salts been analysed, or esters described.

(i) Hydroxyphenanthrenecarboxylic acids,  $[\text{OH} : \text{CO}_2\text{H}]$ .

- 2:3 (?) Yellow needles, m.p. 277° (decomp.); acetate, needles, m.p. 210° (Werner and Kunz, Ber. 1902, 35, 4425); methyl ester, needles, m.p. 126°.  
2:9 Prisms, m.p. 278°; acetate, plates, m.p. 223° (Pschorr and Quade, Ber. 1906, 39, 3123).  
3:2 (?) Yellow prisms, m.p. 303° (decomp.); acetate, needles, m.p. 207°–208°; methyl ester, needles, m.p. 171° (Werner and Kunz, *l.c.*).

(ii) Methoxyphenanthrenecarboxylic acids,  $[\text{OMe} : \text{CO}_2\text{H}]$ .

- 2:9 Colourless needles, m.p. 228° (Pschorr, Ber. 1901, 34, 4002).  
4:9 Needles, m.p. 224° (Pschorr and Jaekel, Ber. 1900, 33, 1827).  
1:10 Yellow leaflets, m.p. 215° (Pschorr, Wolfes and Buckow, Ber. 1900, 33, 169).  
3:10 Needles, m.p. 239° (*ibid.* 174).

(iii) Hydroxyphenanthrenecarboxylic acids,  $[\text{OH} : \text{CO}_2\text{H}]$ .

- 3:4:9 Yellow needles, m.p. 264°; acetate, m.p. 244° (Pschorr and Vogtherr, Ber. 1902, 35, 4414).

(iv) Dimethoxyphenanthrenecarboxylic acids,  $[\text{OMe} : \text{OMe} : \text{CO}_2\text{H}]$ .

- 2:3:9 Needles, m.p. 270° (Pschorr and Buckow, Ber. 1900, 33, 1830).  
3:4:8 Yellow needles, m.p. 211°; acetate, prisms, m.p. 194°–195° (Pschorr, Ber. 1902, 35, 4392; *ibid.* 1907, 40, 1099).  
3:4:9 Needles, m.p. 227°–228° (Pschorr and Summleannu, Ber. 1900, 33, 1819).

(v) Hydroxydimethoxyphenanthrenecarboxylic acids,  $[\text{OH} : \text{OMe} : \text{OMe} : \text{CO}_2\text{H}]$ .

- 3:4:8:9 Six-sided plates, m.p. 231°; acetate, prisms, m.p. 226°–227° (Pschorr, Ber. 1900, 33, 180).  
4:3:6:9 Leaflets, m.p. 254°–256°; acetate, m.p. 201°–203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4409).  
8:3:4:9 Needles; lactone, needles, m.p. 160° (Pschorr and Popovici, Ber. 1906, 39, 3120).

(vi) Dimethoxyphenanthrenecarboxylic acids,  $[\text{OMe} : \text{OMe} : \text{CO}_2\text{H}]$ .

- 3:4:5: Yellow needles, m.p. 235° (Pschorr, Zeidler and Popovici, Ber. 1912, 39, 47; Pschorr

3:4:6:8 Needles, m.p. 201°; methyl ester, needles, m.p. 101°–102°; ethyl ester, leaflets, m.p. 83°–84° (Knorr and Pschorr, Ber. 1905, 38, 3158; Pschorr and Rettberg, Annalen, 1910, 373, 51).

3:4:6:9 Yellow needles, m.p. 203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4406).

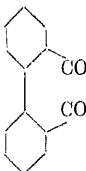
3:4:7:9 Needles, m.p. 214° (Pschorr, Zeidler and Dieckhäuser, *l.c.*).

3:4:8:5 Needles, m.p. 224°–226° (Pschorr and Massaci, Ber. 1904, 37, 2790; Pschorr and Loewen, Annalen, 1910, 373, 70). The 8-ethoxy acid forms needles, m.p. 191°.

3:4:8:9 Leaflets, m.p. 250° (Pschorr and Busch, Ber. 1907, 40, 2003). The 8-ethoxy acid forms leaflets, m.p. 265° (Pschorr and Zeidler, Annalen, 1910, 373, 78).

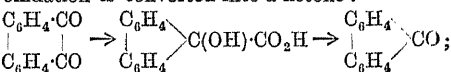
(vii) 3:4-Dimethoxy-5:6-methylenedimethoxyphenanthrene-8-carboxylic acid (Gadamer and Kuntze, Arch. F.

#### DIHYDROPHENANTHRENE DERIVATIVES.



Phenanthraquinone is a typical member of the series of ortho-quinones, but unlike  $[\beta]$ -naphthaquinone, to which it shows a close resemblance in properties, it can be obtained from phenanthrene by direct oxidation.

Phenanthraquinone is formed by the reactions of an ortho-diketone, as may be seen by comparison with benzil; thus it reacts with hot caustic alkali solution, forming a glycollic acid, which by oxidation is converted into a ketone:



yields azines by condensation with ortho-diamines; and gives a mono- and a di-oxime with hydroxylamine. The relationship between the colour and constitution of the dioxime and its derivatives has been discussed by Schmidt and Söll (Ber. 1907, 40, 2454; cf. Hantzsch and Glover, *ibid.* 4344; Schmidt and Mezger, *ibid.* 4560).

Substitution derivatives of phenanthraquinone are formed either by direct substitution of the corresponding phenanthrene derivatives (9-, 10-, or 9:10- compounds), or by direct substitution. In the latter case substitution usually occurs in the equivalent 2- and 7-positions, thus recalling the formation of meta-derivatives of benzene under the directing influence of the carbonyl radicle.

**Preparation.**—Crude phenanthraquinone (100 grams), consisting of the two main constituents of the coal-tar residue, is warmed at 320°–340°, is warmed with potassium dichromate (300 grams) in sulphuric acid (900 grams), diluted with water (1.5 litres), and, after the vigorous reaction has subsided, more dichromate (300 grams) is added. The liquid finally being boiled for precipitation by water the quinone is washed, dried, stirred into concentrated sulphuric acid, and after 24 hours mixed with water. Chromium salts, diphenic acid, acridine, &c., pass into solution, the last traces of organic acids or hydrocarbons being removed by extracting the residue with cold, dilute caustic soda solution, and afterwards (when dry) with ether. The residue is freed from anthraquinone by digestion with warm concentrated sodium bisulphite solution in which the phenanthraquinone dissolves, and the filtrate poured into a solution of potassium dichromate in dilute sulphuric acid;

the precipitate is then washed, dried, and crystallised from alcohol or coal-tar hydrocarbons (Anschütz and Schultz, *Annalen*, 1879, 196, 38). Or it may be made by oxidising purified phenanthrene with chromium trioxide in hot acetic acid solution and purified by means of the sodium bisulphite compound (Graebe, *Annalen*, 1873, 167, 140).

It may be obtained by passing the phenanthrene a current of 1 to 2 amp. per sq. in. through a suspension of phenanthrene in 20 p.c. sulphuric acid, containing about 2 p.c. of cerium sulphate, at 40° (Lucius and Brünig, D. R.-P. 152063; Eng. Pat. 19178 of 1902).

**Properties.**—It crystallises in tufts of long yellow needles, m.p. 205° (Graebe, *l.c.*), boils above 360° without decomposition, sublimes in orange-red prisms, but is odourless and non-volatile with steam. It is only very slightly soluble in water, but dissolves readily in hot alcohol, benzene, or acetic acid. With concentrated sulphuric acid in the cold it gives a green solution, but if benzene containing thiophen be present, the colour is bluish-green, and the liquid, when poured into water and shaken out with ether, gives to the ethereal solution a characteristic reddish-violet colouration, the limit of sensitiveness being reached with 0.0005 gram of phenanthrene (Tschernb. Ber. 1875, 8, 224; *Annalen*, 1879, 196, 38, 2972).

**Reactions.**—(1) Phenanthraquinone, unlike anthraquinone, dissolves in warm sodium bisulphite solution, and is readily reduced to the *hydroquinone* by warming it with sulphurous acid (Graebe, *l.c.*), or sulphuretted hydrogen, or phenylhydrazine acetate (Schmidt and Kämpf, Ber. 1902, 35, 3124).

(2) When boiled with concentrated sulphuric acid it is reduced to phenanthroquinone (Klingemann, Chem. Soc. Trans. 1893, 63, 770).

(3) With hydroxylamine it forms a *monoxime*, golden-yellow needles, m.p. 158° (Meyer and Auwers, Ber. 1889, 22, 1889), and a *dioxime*, yellow prisms, m.p. 202° (Meyer and Auwers, *l.c.*; Schmidt and Söll, Ber. 1907, 40, 2455), apparently without the production of stereoisomerides. The *anhydride* of the dioxime forms colourless needles, m.p. 186°–187° (Schmidt and Söll, *l.c.*).

(4) With phenylhydrazine it gives a *hydrazine*, dark brown needles, m.p. 162°–163° (Zincke, Ber. 1883, 16, 1564; Werner and Frey, *Annalen*, 1902, 321, 304), but in the absence of a solvent the product is phenanthroxazine  $C_{18}H_{17}ON$  (Bamberger and Grob, Ber. 1901, 34, 535).

(5) When boiled with caustic potash solution it is converted into *phenanthroquinone acid* (Friedlaender, Ber. 1874, 7, 123, 134; cf.

Schmidt and Bauer, *ibid.* 1905, 38, 3757), or with caustic alkali solution and permanganate into *diphenyleneketone* (Anschütz and Japp, *ibid.* 1878, 11, 211), but when boiled with methyl alcoholic potash it gives *diphenic acid* (Meyer and Spengler, *ibid.* 1905, 38, 443), or with alcoholic potash *diphenic acid* (Anschütz and Schultz, *Annalen*, 1879, 196, 49) and an orange-coloured *lactone*  $C_{18}H_{13}O_3$ , m.p. 220°–221° (Meyer and Spengler, *l.c.*).

(6) When distilled with soda-lime it yields *diphenyl* (Graebe, *l.c.*), but with caustic lime the products are *diphenyleneketone*, *fluorene alcohol*, and a small quantity of *fluorene* (Anschütz and Schultz, *l.c.*).

(7) With phenols, by prolonged boiling with acetic acid and sodium acetate, it yields additive products which are crystalline and either colourless or yellow (Deichler, D. R.-P. 109344 of 1898).

(8) It forms condensation products with many substances, some of which have been introduced as dyestuffs, but probably have no technical value. For example, it has been condensed with arylhydrazinesulphonic acids. (Akt. f. Anilinfab. D. R.-P. 40745; Eng. Pat. 6688 of 1887); with mono-alkyl- (or aryl)-*ortho*-phenylenediamines (Bad. Anilin- u. Soda-Fab. D. R.-P. 90212; Eng. Pat. 15953 of 1896), or 1:2- or 2:3-diaminoanthraquinone (Bayer & Co. D. R.-P. 170562 of 1904; cf. Scholl and Kärber, Ber. 1904, 37, 4532) forming *azines*; with dialkyl-*p*-aminodiphenylamine, forming *azines* (Bayer & Co. D. R.-P. 126963 of 1901); and with *p*-amino-*m*-hydroxydiphenylamine, forming blue *oxazines* (Fries, D. R.-P. 130733 of 1901).

**Bromo derivatives** (cf. Schmidt, Ber. 1904, 37, 3551). When bromine is added to phenanthraquinone, mixed with sufficient water to form a paste at 0°, a *dibromide*  $C_{18}H_8O_2Br_2$  is formed, m.p. 98° (Schmidt and Junghaus, *ibid.* 1904, 37, 3550), which, when boiled with water, reverts to phenanthraquinone. The *monobromide*, needles, m.p. 233°, is better prepared by brominating the quinone under pressure at 100° (*ibid.* 3358). By further bromination at 150°–160° 2:7-dibromophenanthraquinone, needles, m.p. 323°, is formed.

**Nitro derivatives** (cf. Schmidt, Ber. 1903, 36, 3726). When phenanthraquinone is boiled with concentrated nitric acid for 2 minutes it is converted into a mixture of *phenanthroquinone*, golden yellow scales, m.p. 140° (Anschütz and Schultz, Ber. 1876, 9, 1404; Schmidt and Austin, *ibid.* 1903, 36, 3731), and *phenanthroquinone*, yellow needles, m.p. 140° (Kämpf, *ibid.* 3734). The *phenanthroquinone* is an orange needles, m.p. 140°. It may be converted into 3-nitrophenanthrene by oxidation (Schmidt and Kämpf, Ber. 1902, 35, 3119) or from 9:10-diaminophenanthrene (Austin, Chem. Soc. Trans. 1903, 1132) or from 9:10-diaminophenanthrene (Schmidt and Söll, Ber. 1908, 41, 3684) by nitration.

If phenanthraquinone be further nitrated, the products are 2:7-dinitrophenanthraquinone, yellow needles, m.p. 330° (Schmidt and Söll, 1873, 167, 144; Schmidt and Kämpf, Ber. 1902, 35, 3122; 1903, 36, 3738), and 4:5-dinitrophenanthraquinone, yellow needles, m.p. 330° (Schmidt and Söll, *ibid.* 3735).

(Graeb. zinc (Knesen, D. R.-P. 119001 of 1900).

Schmidt and Bauer (Ber. 1905,

at the ordinary

temperature.

**Amino derivatives.** 2,4,7-triaminophenanthraquinone, violet needles, m.p. 310° (Schmidt and Söll, Ber. 1908, 41, 3694); 2,7-diaminophenanthraquinone, violet needles, m.p. above 310° (Anschütz and Meyer, Ber. 1885, 18, 1944); and 4:5-diaminophenanthraquinone, indistinct crystals, m.p. 235°, which, like 1:8-diaminonaphthalene, does not form condensation products (Schmidt and Kämpf, *ibid.* 1903, 36, 3750), have been described.

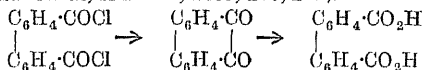
**Hydroxy derivatives.** The amino- and diamino-phenanthraquinones can be diazotised without difficulty, forming the corresponding *phenanthraquinone diazotides* (cf. Werner, Annalen, 1885, 33, 111; Schmidt and Kämpf, *l.c.*; Schmidt and Leipprand, Ber. 1905, 38, 3733). Owing to its relationship to morphine, and the resemblance of some of its properties to those of alizarin, the most interesting of these is:

**Morpholquinone** (3:4-dihydroxyphenanthraquinone). This quinone has been obtained from diacetylmorphol by oxidation, followed by deacetylation (Vongerichten, Ber. 1899, 32, 1521), and from 3-hydroxyphenanthrene by nitration, reduction, and diazotisation (Schmidt and Söll, *ibid.* 1908, 41, 3699). It forms yellowish-brown needles; gives a *diacetate*, yellow needles, m.p. 196°; and, unlike its isomerides and its monomethyl ether, but like alizarin (*q.v.*), forms lakes which with aluminium salts are blue, and with chromium salts deep violet in colour (Vongerichten, *l.c.*). On oxidation it yields *phenanthraquinone*.

#### DIPHENYL DERIVATIVES.

**Diphenic acid** (*diphenyl-2:2'-dicarboxylic acid*).

From the formula of the hydrocarbon, the existence of 15 acids can be predicted, but the acids actually known number only about one-third of these, and of them diphenic acid alone requires description in this article. Diphenic acid is closely related to phenanthraquinone; it was first obtained from this substance by oxidation (Fittig and Ostermayer, Annalen, 1873, 166, 367), and its chloride, on reduction with zinc and hydrochloric acid, forms 9:10-dihydroxyphenanthraquinone or its oxidation product—phenanthraquinone (Graebe and Aubin, Annalen, 1888, 247, 268).



**Preparation.**—A solution of phenanthraquinone (1 part) in sulphuric acid (6 parts) is poured slowly with constant stirring into a solution of potassium dichromate (4 parts) in water (10 parts), whereby the quinone is precipitated in a fine state of division. The heat of dilution of the sulphuric acid is sufficient to start the oxidation, and the reaction is completed by boiling the mixture vigorously during 4 hours in a reflux apparatus; the acid being extracted from the precipitate by sodium carbonate solution (Götze, Monatsh. 1902, 23, 27; Graebe and Aubin, *l.c.*; Schmitz, Annalen, 1878, 193, 116). Diphenic acid also can be obtained

by boiling phenanthraquinone with aqueous or alcoholic potash (Anschütz and Schultz, Annalen, 1879, 196, 49; Meyer and Spengler, Ber. 1905, 38, 443).

**Properties.**—It crystallises in scales or monoclinic prisms, m.p. 228°–229° (Schultz, Annalen, 1880, 203, 97), sublimes in needles, is moderately soluble in hot water, and dissolves readily in alcohol or ether. Dehydrating agents convert it into the *anhydride*; but, when heated with caustic lime, it forms *diphenyleneketone* (cf. Schmitz, *l.c.*; Kerp, Ber. 1896, 29, 228), or with slaked lime or soda-lime, *diphenyl* (Anschütz and Schultz, *l.c.*).

**Derivatives.**—The barium, BaA, 4H<sub>2</sub>O, calcium, CaA, 2½H<sub>2</sub>O, and magnesium, MgA, 4H<sub>2</sub>O, salts are crystalline (Fittig and Ostermayer, *l.c.*). The *dimehyl* ester, conveniently prepared from methyl *o*-iodobenzoate and copper powder (Ullmann, Annalen, 1904, 322, 70), forms monoclinic prisms, m.p. 74·5° (Schultz, *l.c.*), and the *diethyl* ester, cubes, m.p. 42° (Hummel, Annalen, 1878, 193, 129). The *chloride* is crystalline, m.p. 93°–94° (Graebe and Aubin, *l.c.*); the *anhydride* forms needles, m.p. 217° (Anschütz, Ber. 1877, 10, 1184; Graebe and Mensching, *ibid.* 1880, 13, 1302; Graebe and Aubin, *l.c.*); and the *imide*, needles, m.p. 219°–220° (Graebe and Aubin, *l.c.*; Wegerhoff, Annalen, 1889, 252, 16).

**4:4'-Diaminodiphenyl-2:2'-dicarboxylic acid** (*m-diaminodiphenic acid*) is obtained by boiling *m-diaminodiphenylamine* with concentrated hydrochloric acid (Schultz, Ber. 1884, 7, 1069); or, mixed with the 4:2'-dicarboxylic acid, by reducing *m*-nitrobenzoic acid with zinc dust and caustic soda, afterwards extracting the product with hydrochloric acid (Meister, Lucius and Brüning, D. R.-P. 69541 of 1892); or by reducing 4:4'-dinitrodiphenic acid (produceable from 2:7-dinitrophenanthraquinone by oxidation) with tin and hydrochloric acid (Struve, Ber. 1877, 10, 76; Schultz, *l.c.*).

**Properties.**—The acid, H<sub>2</sub>A, 1½H<sub>2</sub>O, forms needles, sparingly soluble in water or alcohol, and the *barium salt* is obtained. From the *tetrazo* compound *disazo* dyes have been made (Paul, D. R.-P. 41819 of 1886; Eng. Pat. 8296 of 1887; Beyer and Kegel, D. R.-P. 44089; 44161 of 1887); but not being direct cotton dyes, they have no technical value. In this respect the disazo dyes from this source differ from those produced by coupling diazotised 4:4'-diaminodiphenyl-3:3'-dicarboxylic acid (*o*-diaminodiphenic acid) with the same naphthylamine- or phenylamine-derivatives, which are direct or longer of any value (D. R.-P. 43524 of 1886; 54662; Eng. Pat. 9676 of 1890). W. P. W.

**PHENANTHRONAPHTHAZINE v. AZINES.**

**PHENANTHROPHENAZINE v. AZINES.**

**PHENAZINE v. AZINES.**

**PHENEGEL v. SYNTHETIC DRUGS.**

**p-PHENETIDINE** may be obtained by the action of sulphuric, or hydrochloric acid, on *p*-phenetidine (Bamberger and Lagutt, Ber. 1885, 18, 1116). It may be prepared by adding 212 grams

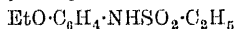
*p*-nitrophenetole gradually to a solution of 848 grams of stannous chloride in 1060 of hydrochloric acid at 50°–60°. It is then precipitated from solution as the hydrochloride by the addition of concentrated hydrochloric acid (Paul, Zeitsch. angew. Chem. 1896, 587).

*p*-Phenetidine may also be prepared by treating phenetole with tin and hydrochloric acid (L. A. P. 3, 3); or by heating benzylidene-*p*-aminophenol with ethyl bromide and alcoholic sodium hydroxide for 3 hours. The product is then warmed with acid when *p*-phenetidine separates (D. R. P. 69006).

*p*-Phenetidine is a liquid, b.p. 254.2°–254.7°, m.p. 2.4° (Schneider, Zeitsch. physikal. Chem. 1896, 19, 155). When heated with hydrogen peroxide and dilute sulphuric acid, it yields a brown colouring matter  $C_{24}H_{22}N_2O_8$ , but when oxidised in the cold with a permanganate it yields quinone, carbon dioxide, acetic and oxalic acids, and resinous substances (Kinzel, Arch. Pharm. 229, 329). When to an alcoholic solution, 5 c.c. of a potassium iodide solution are added and the mixture is heated, a rose-red colour is formed (Goldmann, Pharm. Zeit. 1893, 36, 208). For the detection of phenetidine in urine see Edlfsen, Chem. Zentr. 1900, i. 573.

*p*-Phenetidine sulphonic acid is prepared by heating the hydrogen sulphate of the base or by boiling *p*-nitrophenetole with sodium hydrogen sulphite. It forms readily crystalline sodium salts, and may be diazotised and joined with  $\beta$ -naphthol, thus obtaining the azo-compounds which with barium and aluminium hydroxides form red lakes of great brilliancy and fastness (D. R. P. 146655; see also D. R. P. 189469). *p*-Phenetidine sulphonic acid may also be obtained by heating phenetidine with fuming sulphuric acid (Eng. Pat. 14375, 1897; see also Cohn, Annalen, 1899, 309, 234; Paul, l.c.).

#### Ethyl sulphone phenetidine



is obtained by the action of ethyl sulphate on *p*-phenetidine. It forms leaflets, m.p. 80°–81°, and acts as a monobasic acid, forming well-crystallised salts which may be employed in medicine as they have anti-neuralgic, antipyretic, sedative and hypnotic properties (Autenrieth and Bernheim, Arch. Pharm. 1904, 242, 579). Similar aromatic sulpho derivatives, also employed in medicine, have been prepared (Eng. Pat. 3791, 1896).

By the interaction of *p*-phenetidine and its homologues with ethyl orthoformate, compounds are formed of the type of methenyldi-*p*-phenetidine, which possess anæsthetic properties (Goldschmidt, Chem. Zeit. 1902, 26, 745; J. Soc. Chem. Ind. 1890, 650).

The following derivatives of *p*-phenetidine also have medicinal properties:—

The *citrate*, *tartrate*, and *mandelate* prepared by mixing the theoretical quantities of the acid and base dissolved in suitable solvents (Eng. Pat. 11288, 1895).

*Acetophenin* is prepared by heating *p*-phenetidine with lactic acid (Eng. Pat. 19188, 1894; see also Eng. Pat. 29869, 1896). It forms colourless prisms. The *diacetate* of *p*-phenetidine, m.p. 55°–56°, b.p. 182°/12 mm. is obtained by heating phenacetin (*p*-phenetidine monoacetate) with a

large excess of acetic anhydride (D. R. P. 75611; Bistrzycki and Ulfers, Ber. 1898, 31, 2788; Cohn, *ibid.* 1899, 32, 2239). *Benzyl-p*-phenetidine, m.p. 45°–46°, obtained by heating benzyl chloride with *p*-phenetidine, forms crystalline plates (Zeit. 19, 1753; Wedekind and Fröhlich, Ber. 1907, 40, 1001). *Ethoxyphenyloxamide*  $(CO)_2(NH \cdot C_6H_4 \cdot OEt)_2$  by heating *p*-phenetidine with ethoxy-carbonyl chloride to 140°–145°. It forms thin plates (Wenghöffer, l.c.).

*Amygdulyl phenetidine* by heating *p*-phenetidine mandelate to 170°, forms shining white plates, m.p. 140.5° (Wenghöffer, l.c.). *Ethyl  $\beta$ -phenethyl crotonate* obtained by condensing *p*-phenetidine with ethyl acetoacetate, forms, m.p. 25°–240°, *p*-ethoxy- $\gamma$ -phenethyl crotonate  $CH_3 \cdot CH_2 \cdot CH(CO \cdot OCH_2 \cdot C_6H_4 \cdot OEt) \cdot CH_2 \cdot CH_2 \cdot CO \cdot OCH_2 \cdot C_6H_4 \cdot OEt$ , which has powerful antipyretic properties (Wenghöffer, l.c.). *Salicyl-p-phenetidine* (*Saliphen*), m.p. 142°–143°, is prepared by heating the constituents with phosphorus oxychloride; its *aceto* derivative has m.p. 92° (U.S. Pats. 706355, 706356, 1902; Bolezzi, Gazz. chim. ital. 1898, 28, ii. 197). Also *amino acetyl-p-phenetidine* (*Phenocoll*), *valeryl-p-phenetidine* (*Selatin*), and the *furfural*, *propionyl*, and *aceto-sulphonic* derivatives (J. Soc. Chem. Ind. 1898, 726; Eng. Pat. 14954, 1896; 4565, 1905).

For the *halogen* derivatives, see Staedel (Annalen, 1883, 217, 55); Reverdin (Ber. 1896, 29, 2595); Roverdin and Düring (*ibid.* 1899, 32, 152); Grothe (Arch. Pharm. 1906, 238, 587, 600). Nitro derivatives are described by Wender (Gazz. chim. ital. 19, 218); Autenrieth and Hinsberg (Arch. Pharm. 229, 456); Blanksma (Rec. trav. chim. 1905, 24, 40).

For other derivatives, see Boettinger (Arch. Pharm. 1896, 234, 158); Wirths (*ibid.* 620); Meves (J. pr. Chem. 1900, [ii.] 61, 449); Vorländer (Annalen, 1897, 294, 273, 302); Bischoff (Ber. 1898, 31, 3241, 3248); Partheil and Schumacher (*ibid.* 591); Sachs and Levy (*ibid.* 1904, 37, 874); Schroeter (*ibid.* 1905, 38, 3181); Bischoff and Fröhlich (*ibid.* 1906, 39, 3976); Erlenmeyer (*ibid.* 791); Goldschmidt (Chem. Zeit. 1901, 25, 178); Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123); Fourneau (J. Pharm. Chim. 1910, [vii.] 1, 97).

*o*-Phenetidine is produced as a by-product in the formation of the para-compound.

#### PHENETOLE $C_6H_5 \cdot O \cdot C_2H_5$

*Preparation*.—Phenetole can be obtained by heating potassium phenate with ethyl iodide (Cahours, Ann. Chim. Phys. [iii.] 27, 463), or by heating a mixture of equal parts of phenol and phosphorus pentoxide at 200° and gradually adding alcohol (Kastropp, Ber. 1877, 10, 1685). It is prepared by heating molecular proportions of crude calcium or sodium sulphovinate and sodium phenate (prepared by mixing molecular proportions of phenol and aqueous caustic soda of sp.gr. 1.33) at 150° for some hours (Kolbe, J. pr. Chem. [ii.] 27, 424).

It may also be prepared by fusing perfectly dry sodium ethoxide with perfectly dry phenyl sulphate (Moureu, J. Pharm. Chim. 1898, 8, 211); by the action of sodium ethoxide on triphenyl phosphate (Morel, Compt. rend. 1899, 128, 508); or by passing alcohol into a mixture of

phenol and  $\beta$ -naphthalene sulphonate heated to 120°–140° (D. R.-P. 76574; Fd. l. iv. 18).

*Properties.*—It is a colourless, aromatic liquid, insoluble in water, but soluble in alcohol or ether. It boils at 172° (Cahours), at 171.5°–172.5° at 762.4 mm. (Schiff, *Annalen*, 1883, 220, 105), and melts at –33.5°.

When phenetole is heated with sulphuric acid or left to stand at ordinary temperatures, *p*-phenetole sulphonic acid, together with a little of the meta-acid separates (Shober and Bowers, *Amer. Chem. J.* 1901, 25, 69).

Other sulphur compounds of phenetole are described by Gattermann, *Ber.* 1899, 32, 1136; Taboury, *Bull. Soc. chim.* 1905, [iii.] 33, 836; Smiles and Rossignol, *Chem. Soc. Trans.* 1908, 756.

*Alkyl phenetoles* are obtained by treating a mixture of iodophenetole and ethyl iodide with sodium in benzene solution (Jannasch and Hinrichsen, *Ber.* 1898, 31, 1824).

*p*-Phenetole sulphonic acid,  $C_6H_5 \cdot CH_2 \cdot SO_3H$ , is prepared by oxidizing the dye with cold aqueous permanganate (1431, 1898). It forms orange-coloured microscopic crystals sparingly soluble in cold, readily in hot water.

By reacting with amino compounds a series of phenetole azo-methineazo dyes have been prepared (Green and Sen, *Chem. Soc. Trans.* 1910, 2242; *v.* also *Azo-dyes*).

*Phenetole azo-phenols* have been prepared by Jacobson and Meyer (*Annalen*, 1895, 287, 212); Hewitt, Moore, and Pitt (*Ber.* 1898, 31, 2114; *Chem. Soc. Proc.* 1897, 157); *v.* also Naegeli (*Bull. Soc. chim.* 1894, [iii.] 11, 897).

The following derivatives have also been prepared:—

*Halogen phenetoles* (Autenrieth, *Arch. Pharm.* 1895, 233, 26; Bentley, Haworth, and Perkin, *Chem. Soc. Trans.* 1896, 165; Reverdin, *Ber.* 1896, 29, 2595; Jannasch and Naphtali, *Ber.* 1898, 31, 1714; Grignard, *Compt. rend.* 1904, 138, 1048; Autenrieth and Mühlinghaus, *Ber.* 1906, 39, 4098; Bonneaud, *Bull. Soc. Chim.* 1910, [iv.] 7, 776).

*p*-Iodohydroxy phenetole explodes at 225° and has strong oxidising and antiseptic properties (D. R. P. 161725).

*Nitro-phenetoles* (Lobry de Bruyn, *Rec. trav. chim.* 13, 101; Blanksma, *ibid.* 1904, 23, 119; *ibid.* 1905, 24, 40; *ibid.* 1908, 27, 49; Paul, *Zeitsch. angew. Chem.* 1896, 587; Jacobson and Hönigsberger, *Ber.* 1903, 36, 4124; Blanksma, *Proc. k. Akad. Wetensch. Amsterdam*, 1908, 10, 509; *Chem. Weekblad*, 1908, 5, 789).

*Nitroso phenetoles* (Rising, *Ber.* 1904, 37, 43).  
*Am* ; ; Calhane and Gallivan, *ibid.* 1898, 30, 179; Jackson and Fiske, *ibid.* 1903, 30, 53; Reverdin, *l.c.*)

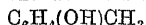
Phenetole also forms compounds with tellurium chloride and with telluric acid (Rising, *Ber.* 1897, 30, 2828; Kunckell, *ibid.* 1895, 28, 609).

For some other derivatives of phenetole *v.* Tust and Gattermann (*Ber.* 1892, 25, 3528); Pechman and Wedekind (*ibid.* 1895, 28, 1688); Wiechell, *Annalen*, 1894, 279, 337; Dzierzowski (J. Russ. Phys. Chem. Soc. 25, 275); Tröger and Volkmer (J. pr. Chem. 1905, [ii.] 71, 236); Tröger and Vasterling (*ibid.* 72, 323).

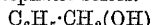
## PHENOCOLL *v.* SYNTHETIC DRUGS.

## PHENOCYANINES *v.* OXAZINE COLOURING MATTERS.

**PHENOL AND ITS HOMOLOGUES.** When a hydroxyl group enters into the molecule of an aromatic hydrocarbon it can do so by replacing (1) a hydrogen atom of the nucleus or (2) a hydrogen atom of a side chain. The isomeric substances thus produced possess, however, very different properties, for, whereas the compound (2) is in all respects analogous to the aliphatic alcohols, the compound (1) exhibits properties which serve to distinguish it entirely from the members of the aliphatic series.



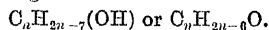
(1)



(2)

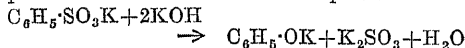
The members of group (1) are therefore classed by themselves, and since the simplest representative of the series,  $C_6H_5 \cdot OH$ , which is produced by the substitution of one hydrogen atom of benzene by hydroxyl, is called phenol, all members of the group are known under the general name of phenols.

*Nomenclature.* According as one, two, three, four, and so forth, hydroxyl groups enter the benzene nucleus, the phenols are termed monohydric, dihydric, trihydric, tetrahydric phenols respectively. Their scientific names may, in every instance, be referred to the parent hydrocarbon, but in many cases, especially as regards the older members of the series, they are generally known by trivial names which are derived from their mode of origin. Thus 1,3-dihydroxybenzene is termed resorcinol from *resorcin*, to orcinol; 1,2,3-trihydroxybenzene is known as pyrogallol because it was originally prepared by the distillation of gallic acid. The phenols possess the general formula

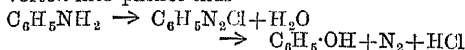


**The Monohydric Phenols.** The simplest members of the series frequently occur among the products of the dry distillation of organic compounds containing oxygen, and therefore phenol, and the cresols occur in coal tar. They may be prepared synthetically by the following processes:—

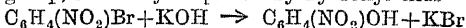
(1) The fusion of a sulphonic acid with potassium hydroxide; thus phenol (potassium salt) is formed from potassium benzene sulphonate in accordance with the equation—



(2) By treating a diazonium salt of an amine with hot water; aniline can be converted into phenol thus—

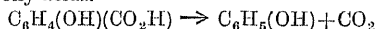


The great stability of the halogen derivatives of the nucleus, which have the halogen atom attached to the carbon atoms of the nucleus, prohibits the formation of phenols by the method usually adopted for the preparation of the aliphatic alcohols, namely by the interaction of halogen derivatives of the hydrocarbon and alkaline hydroxides. If, however, a nitro group is present in the aromatic nucleus, the halogen atom, provided that it is in the ortho- or para- position to the negative group, is readily displaced by hydroxyl thus—

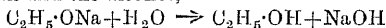


A nitro group in the meta- position has no effect on the inactivity of the halogen atom.

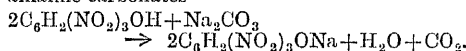
(3) Phenols may also be prepared by eliminating the carboxyl group from aromatic hydroxy acids.



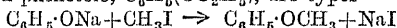
**General properties.** The phenols differ from the aliphatic alcohols in their capacity for forming salts with alkali metals. The corresponding compounds of the aliphatic alcohols, for example sodium ethoxide, are readily and completely dissociated by water, yielding free alkali and the alcohol,



whereas a sodium phenolate or phenate  $C_6H_5\cdot ONa$  dissolves in water without change. The phenols are therefore acid substances which dissolve in aqueous caustic alkalis forming a solution of the salt from which acids reprecipitate the free phenol. The simpler phenols are not, however, acids sufficiently strong to decompose carbonates, but they acquire this property when negative groups are present in the benzene nucleus; thus picric acid dissolves in aqueous alkaline carbonates



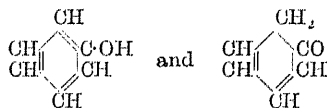
The phenols are therefore weak acids and their alkali salts, which are alkaline to litmus, are readily decomposed by carbonic acid. The action of alkyl iodides on the phenolates yields the phenol ethers, of which anisole,  $C_6H_5(OCH_3)$ , and phenetole,  $C_6H_5(OC_2H_5)$ , are types



The faintly acid character of phenol is illustrated by the behaviour of these compounds since they are decomposed by alkalis, and are therefore

in their properties like the ethers than to the ethereal salts. The hydroxyl group in the phenols is readily displaced by hydrogen by distillation with zinc dust and also by the action of phosphorus trisulphide. It is displaced by halogens through the agency of phosphorus pentabromide or chloride, and by the amino group by heating with zinc ammonium chloride or similar salts. The replacement of the hydrogen atoms of the nucleus takes place with remarkable readiness, and the entrance of halogen atoms, as well as of nitroso, nitro, sulphonic acid, and azo groups, into the molecule of the phenols can be effected with great ease.

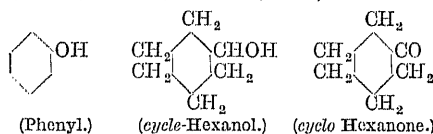
The phenols are characterised by certain colour reactions which may be ascribed to the tendency they possess to react in the tautomeric forms—



Thus well-defined colourations are usually produced by ferric chloride. Other colour reactions are shown by ceric sulphate; for example, sulphuric acid gives a characteristic colour with many phenols; this reaction is the basis of Liebermann's nitroso reaction. Phenols, having free para positions when fused with phthalic anhydride in the presence of a dehydrating agent, yield phthalic anhydride which dissolves in alkali, Vol. IV.—T.

forming strongly coloured solutions. The phenols also combine with diazonium salts yielding coloured oxyazo compounds.

The oxidation of the phenols leads to a variety of products, some produced by the fission of the aromatic ring, as when phenol is converted into oxalic acid by potassium permanganate (Henriques, Ber. 1888, 21, 1619), but more often leading to derivatives of diphenyl by the joining up of two benzene nuclei. The reduction of the phenols could not be effected until Sabatier and Senderens introduced their process of reduction by the aid of nickel at high temperatures. At the present time, practically all the better known phenols have been reduced by this method to the corresponding derivatives of *cyclo*-hexanol. An example may be given in phenol itself which, when its vapour mixed with hydrogen is passed over nickel heated at 215°–230°, is reduced to *cyclo*-hexanol. At the same time, some *cyclo*-hexanone is produced by loss of hydrogen. The mixed product may be either wholly converted into the alcohol by passing it again over nickel at a lower temperature, using a large excess of hydrogen, or into the ketone by passing the vapour without hydrogen over nickel at 330° (compare Compt. rend. 1881, 92, 138, 457, 1257; Brunel, *ibid.* 137, 1268).



### Phenol (Carbolic acid, hydroxybenzene).

Phenol was discovered by Runge in 1834 (Pogg. Ann. 1834, 31, 60; 32, 308) among the products formed by the distillation of coal tar, and was subsequently obtained in a crystalline condition by Laurent (Annalen, 1842, 43, 200). The preparation of phenol from coal tar is described in the article on carbolic acid (*q.v.*); considerable quantities are made synthetically by the fusion of potassium benzene sulphonate with caustic potash in accordance with the general method already mentioned (1). The purification of phenol can be effected by taking advantage of the formation of a crystalline hydrate of the formula  $C_6H_5OH + H_2O$  (m.p. +16°).

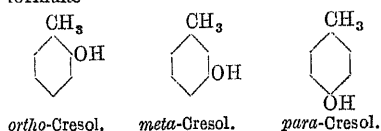
Phenol boils at 183° and solidifies to a mass of large colourless prismatic crystals possessing a characteristic smell. The addition of a small quantity of water to solid phenol causes it to liquefy, since there is formed a solution of water in phenol which is known as 'acidum carbolicum liquefactum.' At the ordinary temperature, about 1 part of water dissolves in 3 parts of phenol. When more water is added an oil separates which ultimately dissolves, yielding a solution of phenol in water; at the ordinary temperature, 1 part of phenol is soluble in 15 parts of water. Phenol is a strong poison, and in its pure condition, or in the form of its concentrated solution, quickly corrodes the skin. It is a powerful aseptic and is employed for this purpose in the form of a 3 per cent aqueous solution. Phenol is used for a variety of purposes; thus it is employed in the preparation of salicylic acid, as well as for the production of



the basis of many colouring matters. The presence of phenol (in the absence of other members of the series) may be detected by the violet colour which is produced by ferric chloride, but a more delicate test is to add bromine water to an aqueous solution of the substance, when even in very dilute solution a flocculent pale yellow precipitate of tribromophenol,  $C_6H_2Br_3(OH)$ , mixed with tribromophenol bromide,  $C_6H_2Br_3 \cdot OBr$ , is at once formed.

*The esters of phenol.* Phenyl hydrogen sulphate,  $C_6H_5 \cdot O \cdot SO_2 \cdot OH$ , is formed as the potassium salt when a concentrated solution of potassium phenolate is treated with potassium pyrosulphate. The salt crystallises from alcohol in small glistening leaflets which dissolve in 7 parts of water at  $18^\circ$ . It is stable towards alkalis but is at once decomposed by acids into phenol and acid potassium sulphate. The free acid is unstable both in alcoholic and in aqueous solution. Potassium phenyl sulphate is of some physiological importance since it is in this form that phenol, taken internally, is excreted. It occurs in small quantity in the normal urine of men and dogs. Phenol methyl ether (anisole *q.v.*)  $C_6H_5 \cdot OCH_3$ , is a pleasant-smelling liquid boiling at  $153.9^\circ$  and melting at  $-37.8^\circ$ . It has sp.gr. 0.990 at  $22^\circ$ . Phenol ethyl ether (phenetole),  $C_6H_5 \cdot OC_2H_5$ , boils at  $170.3^\circ$  and has sp.gr. 0.969 at  $16^\circ$ .

*The Cresols.* The entrance of a hydroxyl group into the molecule of the hydrocarbon toluene can take place either in the side chain or in the aromatic nucleus. In the former event the compound produced is, as already mentioned, aliphatic in character and need not be considered here. It is only when the hydroxyl group enters the aromatic nucleus that the cresols are formed. It is evident that the hydroxyl group can enter in three positions in respect to the methyl group, and hence there are three cresols which may be represented by the formulae

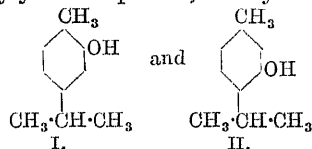


All three cresols occur in coal tar in relatively large quantities, although *o*-cresol is the only member which is isolated, commercially, in a pure condition. Both *o*- and *p*-cresol are prepared in a pure state from the corresponding toluidines through the diazo reaction (method 2). *m*-Cresol is usually derived from thymol by heating it with phosphorus pentoxide. *o*-Cresol (1-methyl-2-hydroxybenzene), melts at  $30^\circ$  and boils at  $190.8^\circ$ . *m*-Cresol (1-methyl-3-hydroxybenzene), melts at  $4^\circ$  and boils at  $202.8^\circ$ . *p*-Cresol (1-methyl-4-hydroxybenzene), melts at  $36^\circ$  and boils at  $201.8^\circ$  (B.P.).

The six possible *xilenols* (dimethylhydroxybenzenes) have been prepared either from the corresponding xyldines or from the isomeric xylene sulphonic acids by fusion with potash: *adj-o-xylénol* (1:2-dimethyl-3-hydroxybenzene), melts at  $73^\circ$  and boils at  $218.5^\circ$ ; *1:2-dimethyl-4-hydroxybenzene*, melts at  $65^\circ$  and boils at  $222^\circ$ ; *adj-m-xylénol* (1:3-dimethyl-2-hydroxybenzene),

melts at  $49^\circ$ ; *asym-m-xylénol* (1:3-dimethyl-4-hydroxybenzene), melts at  $25^\circ$  and boils at  $209^\circ$ ; *sym-m-xylénol* (1:3-dimethyl-5-hydroxybenzene), melts at  $63^\circ$  and boils at  $218^\circ$ ; *p-xylénol* (1:4-dimethyl-2-hydroxybenzene), melts at  $75^\circ$  and boils at  $209^\circ$ . The three more important trimethylhydroxybenzenes are: *mesitol* (1:3:5-trimethyl-2-hydroxybenzene), melting at  $75^\circ$ ; *eudocumenol* (1:2:4-trimethyl-5-hydroxybenzene), which melts at  $25^\circ$ ; and *hemelliténol* (1:2:3-trimethyl-5-hydroxybenzene), melting at  $81^\circ$ . *Prehnitenol* is 1:2:3:4-tetramethyl-5-hydroxybenzene; it melts at  $86^\circ$ – $87^\circ$  and boils at  $266^\circ$ . *Durenol*, which is 1:2:4:5-tetramethyl-3-hydroxybenzene, melts at  $117^\circ$  and boils at  $249^\circ$ – $250^\circ$ .

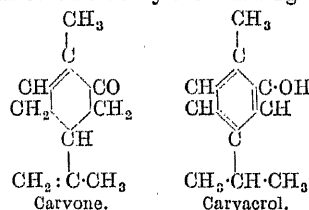
Two important substances are included among the higher phenols, namely *carvacrol* and *thymol*. These compounds occur naturally in many ethereal oils and are related to the terpenes and camphors. They are both monohydric phenols derived from cymene (1-methyl-4-isopropylbenzene), and since this hydrocarbon can only yield two phenols, namely



it is evident that one must be thymol and the other carvacrol.

The structure of the two compounds is revealed by the fact that when heated with phosphorus pentoxide, carvacrol yields propylene and *o*-cresol; its constitution is therefore represented by formula (I.). Thymol, on the other hand, yields propylene and *m*-cresol under the same conditions and must therefore have the structure represented by formula (II.).

*Carvacrol* (1-methyl-4-isopropyl-3-hydroxybenzene), occurs in the essential oils of *Thymus hirtum* and *Satureja hortensis*, and also in small quantity in the oil of *Thymus serpyllum*. It may be prepared by fusing sodium cymene with caustic soda and can be extracted from the acidified product by means of ether. It is readily formed from its isomeride carvone, a constituent of cumin oil, either by heating with caustic potash or by the action of phosphoric acid. The relation between these substances is shown by the following formulæ—



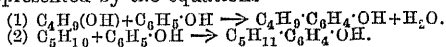
It is also derived from camphor by the action of iodine. Carvacrol is a thick liquid which boils at  $237^\circ$ ; it solidifies when cooled and melts at  $+0.5^\circ$ . It gives a green colouration with ferric chloride in dilute alcoholic solution.

*Thymol* (1-methyl-4-isopropyl-3-hydroxybenzene), occurs in the essential oils of the common

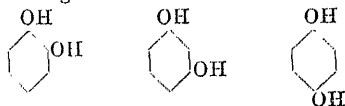
garden thyme, *Thymus vulgaris*; of *Ptychotis ajowan*; and of horsemint, *Monarda punctata*, as well as in the essential oil of *Thymus serpyllium*. It may be obtained by shaking oil of thyme with aqueous caustic soda, separating the undissolved terpenes, and acidifying the alkaline extract with hydrochloric acid. The precipitated thymol is then recrystallised from acetic acid.

Thymol forms large transparent crystals, soluble in 1100 parts of water at 16°. It is readily volatile with steam, but the aqueous solution is not coloured by ferric chloride. It melts at 50° and boils at 232°. It is a valuable aseptic and can, since it is less poisonous than phenol, be taken internally. When an aqueous solution of thymol is treated with a half part of acetic acid and then with one part of sulphuric acid and warmed, a red-violet colour is produced.

A reaction by which certain higher monohydric phenols can be produced has been introduced by Liebermann (Ber. 1881, 14, 1842). It is carried out by treating aliphatic alcohols with phenol in the presence of zinc chloride. Thus *p*-isobutylphenol (4-isobutyl-1-hydroxybenzene) can be prepared by heating phenol (10 parts), isobutyl alcohol (8 parts), and zinc chloride (24 parts) at 180°. It crystallises in needles, melts at 97.4°–98° and boils at 236°–238°. A similar reaction has been discovered by Königs (Ber. 1890, 23, 3145), only in this case the olefinic hydrocarbons are treated with phenol in the presence of a mixture of one part concentrated sulphuric acid and nine parts of glacial acetic acid. The two reactions may be represented by the equations—



**The dihydric phenols.** The formula of benzene permits of the existence of three isomeric dihydroxy derivatives; their names and formulæ are given below



As products of the decomposition of naturally occurring substances, these dihydric phenols have been known from the earliest times; their orientation was first suggested by Petersen (Ber. 1873, 6, 308; 1874, 7, 58).

**Pyrocatechol** (1:2-dihydroxybenzene), was first obtained by Reinsch in 1839 (Ber. 20, 301) by the dry distillation of catechin (*Mimosa catechu*). It is obtained by the distillation of catechins and is frequently prepared by the distillation of certain vegetable substances which give a green colour with ferric salts (Wagner, Annalen, 1850, 76, 351; Uloth, *ibid.* 1859, 111, 215). It is, moreover, formed in the distillation of wood and is therefore present in crude pyroligneous acid.

**Preparation.** (1) Pyrocatechol can be made from its methyl ether, *guaiacol*, which is the chief constituent of the fraction of beech wood tar which boils at 200°–205°. The hydrolysis can be effected and a yield of 70 p.c. obtained by the following process (Hartmann and Gattermann, Ber. 1892, 25, 3532). 15 grms. of guai-

acol, cooled from without by ice, are gradually mixed with 12 grms. of aluminium chloride and then heated in an oil bath for 2 hours at 210°. At the end of this time the product, which is a hard solid cake, is removed from the flask, ground to powder and warmed with dilute hydrochloric acid, by which process the soluble pyrocatechol is removed from unchanged guaiacol and resinous products. The aqueous extract is then saturated with common salt and the phenol extracted by ether. Pyrocatechol remains on evaporating the solvent and is purified by distillation.

According to Perkin (Chem. Soc. Trans. 1890, 57, 587), an almost quantitative yield of pyrocatechol can be obtained from guaiacol by the following means. A solution of guaiacol in 1.5 times its weight of fuming hydriodic acid (sp.gr. 1.96) is gently heated for about an hour in an apparatus fitted with a reflux condenser (to condense the eliminated methyl iodide), allowed to cool, mixed with a fourth of its weight of hydriodic acid and heated as before for 1 hour. The product, after washing with water, is extracted by ether, the ether removed by distillation and the residual oil purified by rapid fractionation.

(2) Pyrocatechol may be obtained in a pure condition by fusing phenol with sulphuric acid with 24 molecular proportions of caustic potash at 320°–330°; the yield is 20 p.c. of the theoretical. By using less potash or a lower temperature a smaller yield is obtained.

Pyrocatechol crystallises from benzene as glistening colourless plates which melt at 104°; it boils at 240° and is slowly volatile with steam. 31.1 parts are soluble in 100 parts of water at 20°, and the aqueous solution gives a green colouration with ferric chloride, which changes to violet on the addition of sodium carbonate or acetate; this reaction is characteristic of the dihydric derivatives of benzene. The solution gives a green colour with lead acetate, and the potassium salt, which is insoluble in water, is used for the quantitative estimation of the phenol. The salt can be dried at 100°–110°, and has the composition  $\text{C}_6\text{H}_4\text{O}_5\text{Pb}$ .

**Derivatives of pyrocatechol.** The ethers of pyrocatechol are of considerable importance, and many natural products are derivatives of the methyl ethers and especially of the methylene ether (*v. Ptereronal*).

**Guaiacol**  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$ , was originally prepared by the distillation of guaiacum resin (Unverdorben, Pogg. Ann. 1826, 8, 402), and is also obtained in large quantities by the distillation of wood. It is best derived from the fraction of beechwood tar, boiling at 200°–220° by the following process (Hlasiwetz, Annalen, 1858, 106, 339). The fraction is repeatedly shaken with moderately strong ammonia, then washed with water and rectified. The product is then dissolved in an equal volume of ether, and the potassium salt, which separates on the addition of a slight excess of alcoholic potash, is washed with ether and freed from alcohol, and finally decomposed with sulphuric acid. Guaiacol may be obtained synthetically by direct methylation, for which purpose molecular quantities of pyrocatechol, caustic potash, and potassium methyl sulphate are heated at 170°–

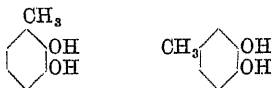
180° (Gorup, *Annalen*, 1868, 147, 248; Béhal and Choay, *Bull. Soc. chim.* 1893, [iii.] 9, 142).

The barium salts of guaiacol and creosol (the mono-methyl ether of homo-catechol, 3:4-dihydroxy-1-methylbenzene) are much less soluble in water than those of the admixed phenols, and a process for the separation of them is being worked depending on this property, hitherto not technically (D. R. P. 56003, 90). Beechwood tar (40 kilos.), is mixed with barium hydroxide (64 kilos.) and 150 litres of hot water. On cooling, the crystalline magma is filtered off, pressed, washed once with water, and the guaiacol, which is mixed with more or less creosol, separated by the addition of hydrochloric acid and subsequently steam distilled. The distillate, on treatment with aqueous potash, gives the sparingly soluble salts of guaiacol and creosol, the two phenols being finally separated by distillation.

Guaiacol has only within comparatively recent times been obtained in a chemically pure condition (Béhal and Choay, *Bull. Soc. chim.* 1893, [iii.] 9, 142). It melts at 28.5° and boils at 205°, dissolves in 60 volumes of water at 15°, and has sp.gr. 1.143 at 15°. A 1 p.c. solution in alcohol gives a blue colouration with ferric chloride, changing quickly through green to yellow. When heated with phosphorus pentachloride it is converted into *o*-chloranisole; a reaction by which its relationship with pyrocatechol and its orientation was originally determined (Fishli, *Ber.* 1878, 11, 1461).

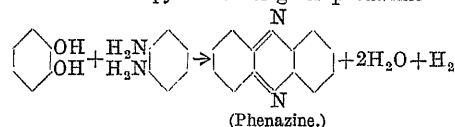
**Veratrole**  $C_8H_8(OCH_3)_2$  (pyrocatechol dimethylether, 1:2-dimethoxybenzene) is obtained by the distillation of veratric acid with baryta and also by the methylation of the potassium salt of guaiacol. It melts at 22.5°, boils at 205°, and has sp.gr. 1.081 at 21.2°.

**Other ortho-dihydric phenols.** Two methyl derivatives can be derived from pyrocatechol by the entrance of a methyl group into the benzene ring, namely

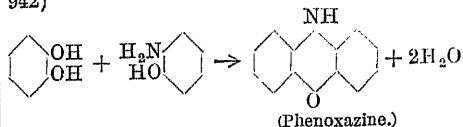


The first is *isohomopyrocatechol*, 2:3-dihydroxy-1-methylbenzene, which melts at 47° and boils, with partial decomposition, at 238°–240°. The second is *homocatechol*, 3:4-dihydroxy-1-methylbenzene, melting at 51° and boiling at 251°–252°. The methyl ether of this substance, *creosol* (4-hydroxy-3-methoxy-1-methylbenzene), accompanies guaiacol as a constituent of beechwood tar; it boils at 221°–222° and has sp.gr. 1.111 at 0°.

**Reactions of ortho-dihydric phenols.** Apart from the special reactions already mentioned, the ortho-dihydroxy derivatives of benzene are characterised by the following properties. When treated with *o*-phenylenediamine they yield phenazines or derivatives of this substance. Thus pyrocatechol gives phenazine

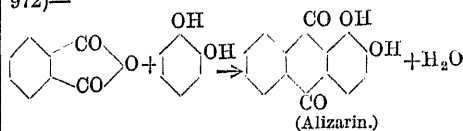


(*Ris*, *Ber.* 1886, 19, 2206). With *o*-aminophenols they yield phenoxazines, as is illustrated by the formation of phenoxazine from pyrocatechol and *o*-aminophenol (Bernthsen, *ibid.* 1887, 20, 942)



They also yield phenoxazines when treated with *o*-aminophenol (*ibid.* 1887, 19, 3255).

Other typical condensations may be illustrated by the formation of alizarin from phthalic anhydride and pyrocatechol with sulphuric acid (Baeyer and Caro, *Ber.* 1876, 7, 972)—



and by the production of a phthalein from pyrocatechol and phthalic anhydride in the presence of zinc chloride at 140° (Baeyer and Kochendörfer, *Ber.* 1889, 22, 2196).

**Resorcinol**  $C_6H_4(\text{OH})_2$  (Resorcin, 1:3-dihydroxybenzene) was first obtained by Hlasiwetz and Barth (*Annalen*, 1864, 130, 351) by treating certain resins (galbanum, &c.) with caustic soda, and is soluble in all resins which are soluble in caustic soda. On dry distillation react in this manner (*cf. ibid.* 1866, 139, 83, 100). Resorcinol can also be obtained from benzenedisulphonic acids, halogensulphonic acids and halogenphenols; it is prepared on the technical scale from sodium resorcinate by fusion with caustic soda (*Engl. poly. J.* 1887, 263, 154).

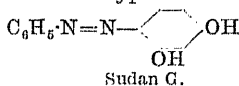
benzene is thus described by Hlasiwetz and Busch (*Mon. Sci.* 1864, 11, 1137). To prepare resorcinol, 90 kilos. of fuming sulphuric acid are placed in a cast-iron vessel provided with a stirring apparatus, and attached to a reflux condenser, and 24 kilos. of pure benzene are gradually run in with constant stirring; the temperature gradually rises to the boiling-point of benzene, and in the course of two to three hours the benzene is completely converted into the benzenedisulphonic acid. The reflux condenser is then removed, the vessel attached to a condenser arranged in the ordinary way, and the temperature raised to 275° in order to convert the benzenedisulphonic acid into the disulphonic acid. The water which comes off with the water stage of the reaction is collected in the receiver. After heating for about 20 minutes at this temperature, the mass is allowed to cool, then poured into 2000 litres of water, neutralised with milk of lime, and converted into the sodium salt in the usual way, the solution of the salt being subsequently evaporated to dryness. To obtain resorcinol from this product, 60 kilos. of the completely dry sodium salt are added to 150 kilos. of caustic soda dissolved in the smallest possible quantity of water, and the mass heated at 270°

in a cast-iron vessel with continual stirring for from 8 to 9 hours, at which time it becomes gradually finally solid. On cooling, it is dissolved in 500 litres of boiling water, the solution acidified with hydrochloric or sulphuric acids and boiled until all sulphur dioxide has escaped. The tarry matter, which is deposited, is filtered off from the cold solution, and the filtrate thoroughly extracted with ether in a copper extraction apparatus, the ether being subsequently distilled off and recovered. The crude resorcinol, obtained in this manner, is a colourless crystalline mass, which can be freed from traces of ether and water by heating it in an enamelled vessel at 215°. It then forms a hard brittle mass containing 92-94 p.c. of resorcinol together with some phenol and about 5 p.c. of tarry matter. To free it from these impurities it is distilled, water coming over first, then phenol and finally resorcinol. It can be further purified by sublimation or recrystallisation from benzene. Resorcinol may also be prepared from *m*-aminophenol through the diazo compound (Bartlin, Ber. 1878, 11, 2101).

Resorcinol crystallises from benzene in large colourless needles which melt at 119°; it boils at 276.5°, and is slowly volatile with steam: 100 parts of resorcinol dissolve in 67.9 parts of water at 12.5°. The aqueous solution gives a dark violet colour with ferric chloride which is discharged on the addition of sodium acetate. It gives no precipitate with lead acetate and can, by this means, be distinguished from pyrocatechol. Resorcinol gives a voluminous precipitate of tribromoresorcinol with bromine water and reduces both ammoniacal silver nitrate solution and Fehling's solution when warmed. On fusion with potash it is converted into a mixture of phloroglucinol (60-70 p.c.), and dioresorcinol (1.5 p.c.) (Ber. 1881, 12, 503).

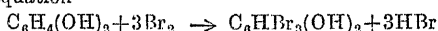
When fused with phthalic anhydride, resorcinol is converted into fluorescein and the presence of small quantities can be detected by means of this reaction. The test is best effected by dissolving the substance in dilute ammonia and pouring the solution into a large volume of water, when the presence of resorcinol is indicated by the formation of a yellow solution having a fine green fluorescence.

Resorcinol and its analogues (the aminophenols, &c.) are extensively used in the preparation of colouring matters (see PYRONINE COLOURING MATTERS). It combines with diazonium salts forming oxyazo colouring matters of which Sudan G is a type



but these compounds have little technical importance.

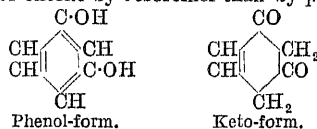
Resorcinol may be estimated quantitatively by titration with bromine water or by means of a solution of bromine in alkali, as in the case of phenol. The method is based on the formation of tribromoresorcinol in accordance with the equation



Delicate tests for resorcinol are described by

Carobbio (Chem. Zentr. 1906, [ii.] 632) and by Silbermann and Ozorovitz (*ibid.* 1908, [ii.] 1022).

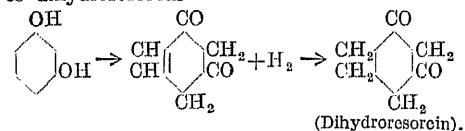
*General properties of the meta-dihydric phenols.* The tendency for the phenols to react in the keto (hydroaromatic) form increases with the entrance of hydroxyl groups in the meta-position. This tendency is therefore exhibited to a greater extent by resorcinol than by phenol



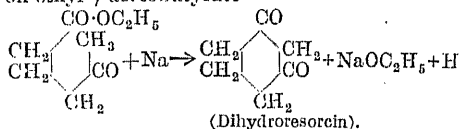
and is shown to a much greater degree by phloroglucin (*g.v.*).

Although the keto form of resorcinol is not sufficiently stable to cause this substance to react with the usual ketonic reagents (hydroxylamine, &c.), yet there is no doubt that the formation of  $\alpha$ -alkyl derivatives by the action of alkyl iodides on the sodium salt of resorcinol (*cf.* Herzog and Zeisel, Monatsh. 1889, 12, 191, 368; Ciamician and Silber, Gazz. chim. ital. 1893, 22, 2, 56) is due to the phenol reacting in its keto form.

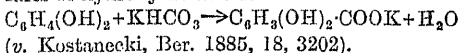
It has, moreover, been found by Merling (Annalen, 1893, 278, 20) that, unlike phenol, resorcinol is readily reduced by sodium amalgam to dihydroresorcin



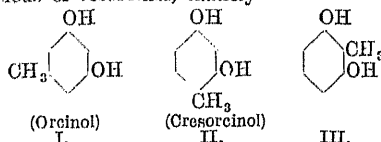
a typical alicyclic diketone which has been prepared by Vorländer (Ber. 1897, 28, 2348; Annalen, 1897, 294, 269) by the action of sodium on ethyl- $\gamma$ -acetoxybutyrate



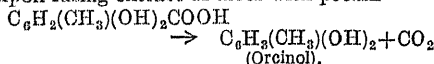
The meta-dihydric phenols also react with aqueous alkaline bicarbonates, yielding the salts of hydroxy acids thus—



*Homologues of resorcinol.* There are three possible dihydroxytoluenes which can be formed by the entrance of a methyl group into the nucleus of resorcinol, namely—



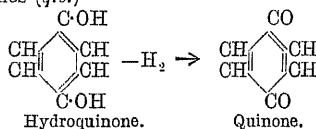
**Oreinol** (3:5-dihydroxy-1-methylbenzene) was discovered by Robiquet in 1820, and is found in many lichens (*Rocella tinctoria*, *Lecanora*, &c.). It is formed by the elimination of carbon dioxide from orsellinic acid, *e.g.* upon fusing extract of aloes with potash—



and can also be prepared synthetically from toluene (Ber. 1882, 15, 2992). It is also formed by the action of sodium on ethyl acetouedicarboxylate (*ibid.* 1886, 19, 1446).

Orcinol crystallises from water in prisms containing water of crystallisation which begin to melt at about 56° in their hydrated state; when anhydrous it melts at 107°–108°. It gives a violet-black colouration with ferric chloride, but does not yield a phthalein when fused with phthalic anhydride. In alkaline solution, when warmed, it gives a bright-red liquid which shows a strong yellowish-green fluorescence on dilution (homofluorescein reaction). *Cresorcinol* (2:4-dihydroxy-1-methylbenzene, formula II.), m.p. 100°, b.p. 267°–270°; *2:6-dihydroxy-1-methylbenzene*, formula III., melts at 63°–66°. Both the above compounds give the fluorescein reaction. *p-Xylorcinol* ( $\beta$ -orcinol, 3:5-dihydroxy-1:4-dimethylbenzene), is formed by the decomposition of *isochlorogenic acid*; it melts at 163° and boils at 277°–280°.

**Hydroquinone**  $C_6H_4(OH)_2$ . (Quinol, 1:4-dihydroxybenzene). The para-dihydroxy derivatives of benzene possess the property of readily losing two atoms of hydrogen in the presence of oxidising agents and passing into quinones (*q.v.*)—



They are therefore named hydroquinones. Hydroquinone was first prepared by Caventou and Pelletier from quinic acid on dry distillation, and was further investigated by Wöhler (Annalen, 1844, 51, 145). It occurs naturally in the sugar-bush (*Protea mellifera*), a shrub of common occurrence in South Africa (Hesse, *ibid.* 1896, 290, 317). It can be prepared synthetically by a number of processes, of which the following are the more important. From phenol by oxidation with alkaline potassium persulphate (D. R. P. 81068, 1895; Chem. Fabrik. vorm. E. Schering); by fusing *p*-iodophenol with potash (Körner, Zeitsch. physikal. Chem. 1866, 662, 731); and from *p*-diazophenol sulphate when boiled with 10–15 p.c. sulphuric acid (Weselsky and Sehuler, Ber. 1876, 9, 1159). It is also formed when the *ortho*-sulphate is hydrolysed by boiling (Kawaler, Annalen, 1855, 185, 186).

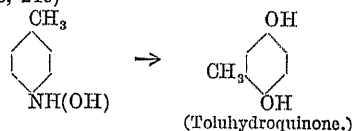
*ibid.* 1858, 107, 228) and is produced by the electrolytic oxidation of benzene in alcohol-sulphuric acid solution (Gattermann and Friedrichs, Ber. 1894, 27, 1942). It has been prepared from ethyl succinate through ethyl succinosuccinate (Hermann, Annalen, 211, 336).

The preparation of hydroquinone is best effected by the oxidation of aniline in the following way. A concentrated solution of sodium dichromate is added to a well-cooled (5–10 p.c.) solution of aniline in 8 parts of sulphuric acid and 25 parts of water. The mixture at first becomes green, and towards the end of the operation, deep blue-black; a further addition of the dichromate solution brings about the solution of the greater part of the precipitate, and a brown, turbid

liquid is obtained containing quinone and quinhydrone in suspension. The quinone and quinhydrone are then reduced to hydroquinone by passing sulphur dioxide through the liquid until it smells of sulphurous acid, the suspended matter is filtered off, and the hydroquinone extracted from the filtrate by means of ether, which is subsequently distilled off. The yield of crude hydroquinone under these conditions amounts to as much as 85 p.c. In order to purify the product it is dissolved in the smallest possible amount of water, the solution boiled with animal charcoal and a little sulphurous acid, filtered and allowed to crystallise.

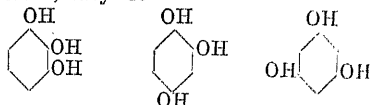
Hydroquinone is dimorphous. It crystallises from water in colourless hexagonal prisms which, on heating, sublime in monogonic scales, m.p. 115° (730 mm.); 100 parts of a solution of hydroquinone saturated at 15° contain 5.85 parts of the phenol and it is readily soluble in alcohol, ether, and in hot water. Ferric chloride converts it into quinone and quinhydrone, and an aqueous solution gives no precipitate with lead acetate. Its alkaline solution becomes brown on exposure to the air. It reduces Fehling's solution in the cold and ammoniacal silver nitrate solution on warming, owing to the formation of quinone, and this oxidation to quinone is effected by nitric acid, chlorine or other oxidising agents. When its vapour is passed through a tube heated to redness, it is transformed into quinone and free hydrogen (Hesse, Annalen, 1860, 114, 297). When heated with phthalic anhydride and sulphuric acid it yields quinazarin, and when heated with phthalic anhydride and zinc chloride it is converted into the colourless hydroquinonephthalein (Grimm, Ber. 1873, 6, 506).

**Homologues of hydroquinone** are usually named after the parent hydrocarbon. *Toluihydroquinone*,  $C_6H_3(CH_3)(OH)_2$  (2:5-dihydroxy-1-methylbenzene), is of interest because it is formed by the action of hot dilute sulphuric acid on *p*-tolylhydroxylamine (Bamberger, Ber. 1895, 28, 246)—

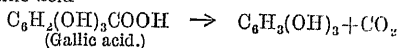


It melts at 125°. Of the *xylohydroquinones*, the *ortho*-compound melts at 221°, the *meta*-compound at 149°, and the *para*-derivative at 211°.

**The trihydric phenols.** The three theoretically possible trihydroxy derivatives of benzene are known; they are



**Pyrogallol**,  $C_6H_3(OH)_3$  (pyrogalllic acid, 1:2:3-trihydroxybenzene), was first prepared by Scheele in 1786 by the dry distillation of gallic acid—



and it is by this process that it is prepared



obtained from *Spartium scoparium* (Hlasiwetz, *ibid.* 1866, 138, 190). It is also obtained by fusing benzene trisulphonic acid, phenol (Barth and Schreder, Ber. 1879, 12, 422), resorcinol (Barth and Schreder, *ibid.* 1879, 12, 503), or orcinol (Barth and Schreder, Monatsh, 1882, 3, 649) with an excess of caustic soda. It has been prepared synthetically from ethyl malonate by Baeyer (Ber. 1885, 18, 3458); compare also Moore (Chem. Soc. Trans. 1904, 85, 165).

**Preparation.** It is best prepared by fusing resorcinol for about 25 minutes with 6 parts of caustic soda at a gradually increasing temperature until the vigorous evolution of gas, which soon sets in, almost ceases and the mass becomes a bright chocolate colour. The mass is then dissolved in water and the solution acidified with dilute hydrochloric acid, filtered, and extracted with ether; the ether being subsequently distilled off, and the phloroglucinol, which separates as a magma, recrystallised after purification with animal charcoal (Barth and Schreder, *l.c.*).

The product usually contains some resorcinol, which can be removed by heating at 100° and moistening with water from time to time until all the resorcinol has been sublimed (Tiemann and Will, Ber. 1881, 14, 954).

Phloroglucinol can be completely freed from resorcinol and diresorcin by boiling with a concentrated aqueous solution of potassium bicarbonate. Under these circumstances, the potassium salt of phloroglucinolcarboxylic acid is formed which crystallises in needles, is sparingly soluble in a solution of potassium carbonate and alcohol, and when added to dilute hydrochloric acid gives the free acid which can be extracted with ether. The crystalline acid obtained by evaporating the ether solution eliminates carbon dioxide when boiled with water, pure phloroglucinol remaining in the solution (Will and Albrecht, Ber. 1884, 17, 2103; Will, *ibid.* 1885, 18, 1323; Skraup, Monatsh. 1889, 10, 721).

According to Brunner (Annalen, 1907, 351, 313), potassium phloroglucinolcarboxylate is formed at the ordinary temperature when a stream of carbon dioxide is passed through a mixture of the phenol and potassium carbonate in glycerol.

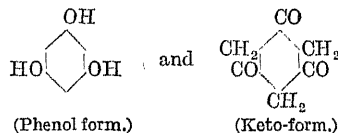
Phloroglucinol crystallises from water in colourless tables containing 2H<sub>2</sub>O, and from ether in large rhombic plates. These lose their water of crystallisation at 100°, forming the anhydrous form, which melts at 217°-219° when rapidly heated, but at 200°-209° when slowly heated (Baeyer, Ber. 1886, 19, 2186). It sublimes without decomposition, has a sweet taste, reduces Fehling's solution, is readily soluble in water, alcohol, and in ether, and, according to Tiemann and Will (*l.c.*), is more readily extracted from a neutral than from an acid solution. It is a dibasic acid (Thiele and Roemer, Zeitsch. physikal. Chem. 1908, 63, 711) and its alkaline solution absorbs oxygen from the air, but less readily than pyrogallol (Weyl and Goth, Ber. 1881, 14, 2673). Its aqueous (concentrated) solution gives a blue-violet colour with ferric chloride.

When potassium nitrate is added to a very dilute solution of phloroglucinol and aniline nitrate, a cinnabar-red precipitate of benzene-

azophloroglucinol is formed after a short time (Weselsky, Ber. 1875, 8, 967; Weselsky and Benedikt, *ibid.* 1879, 12, 226), a distinct precipitate being obtained at the end of 3 hours with only 0.0005 gm. of the substance. A similar reaction is, however, produced by maclurin, decoction of fustic, catechin, and extract of hops (Weselsky, *ibid.* 1876, 9, 217).

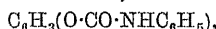
Phloroglucinol in the presence of hydrochloric acid gives a red-violet colour with woody substances; thus a solution containing 0.01 p.c. of phloroglucinol, when mixed with moistened shavings of wood, gives a red, and a solution containing no more than 0.001 p.c. will give this reaction if the shavings are allowed to remain in the solution for 24 hours (Wiesner, Dingl. poly. J. 1878, 227, 397; Kiellmeyer, *ibid.* 584; Wagner, *ibid.* 1878, 228, 173). Phloroglucinol solution (1-30000) gives a definite colour with woodpulp paper (Cross, Bevan and Briggs, Ber. 1907, 40, 3119). Unlike pyrogallol, phloroglucinol is not poisonous.

**The desmotropism of phloroglucinol.** It has been already stated that the increase in the number of hydroxyl groups in the meta-positions in the benzene nucleus increases the tendency for the compound to react in its desmotropic forms. It is therefore to be expected that in phloroglucinol this tendency would be at its maximum. The experimental facts which show that this phenol reacts in the two desmotropic forms

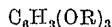


may be summarised as follows:—

The *phenol form* leads to the formation of a tricarbanilido derivative,

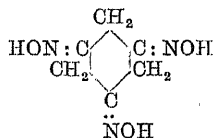


when phloroglucinol is treated with phenylisocyanate (Goldschmidt and Meissler, Ber. 1890, 23, 269) and causes the phenol to yield well-defined o-alkyl derivatives of the type

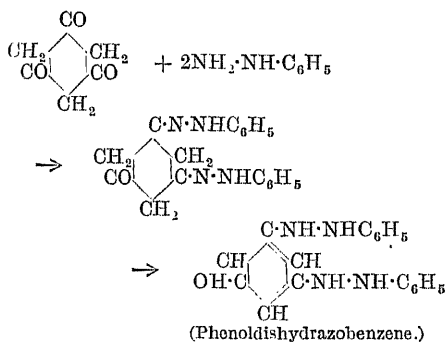


when it is alkylated under suitable conditions (Benedikt, Annalen, 1875, 178, 97; Will and Albrecht, Ber. 1884, 17, 2107; Herzog and Zeisel, Monatsh. 1888, 9, 218; Hesse, Annalen, 1893, 276, 328).

The *keto-form* leads to the production of a trioxide

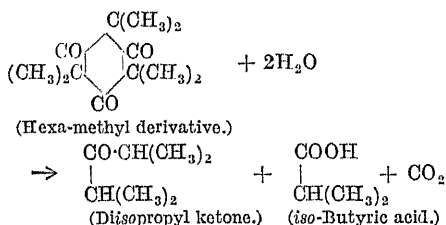


when phloroglucinol is treated with hydroxylamine (Baeyer, Ber. 1886, 19, 159). It is a sandy, crystalline powder which decomposes with explosive violence at 155°. The action of phenylhydrazine leads, in the first instance, to the formation of a salt which on long standing in alcohol passes into phenoldis-

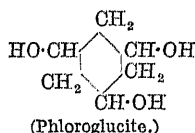


(Baeyer and Kochendoerfer, Ber. 1889, 2189). The keto-form is also shown by the readiness with which phloroglucinol reacts with concentrated aqueous ammonia in the cold, yielding, firstly, aminophenol (Chlorophenol 2:5:6-trihydroxy-1-aminobenzene) and, secondly, phenoldishydrazobenzene (Monatsh. 1893, 14, 401).

Tetra-, penta-, and hexa-alkylated products are formed from phloroglucinol when it is alkylated by alkyl iodides in the presence of alcoholic potash. The alkyl groups in these compounds are not removed by hydriodic acid and are therefore attached to carbon. Their constitution may be illustrated by the hexamethyl derivative which, on heating with concentrated hydrochloric acid at 190°, is transformed into carbon dioxide, diisopropyl ketone, and isobutyric acid,

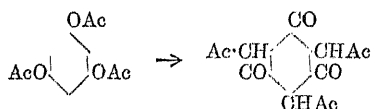


(Horzig and Zeisel, Monatsh. 1888, 9, 217, 882; 1889, 10, 735; 1893, 14, 376). Phloroglucinol is reduced by sodium amalgam in the cold, yielding phloroglucite (cyclo-hexanetriol)



(W. Wislicenus, Ber. 1894, 27, 357).

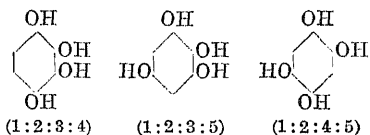
The tendency for derivatives of the phenol form to pass into derivatives of the keto-form is illustrated by the behaviour of phloroglucinol-triacetate which, on heating with an equal part of zinc chloride for 3 hours at 130°, passes into triacetotriketohexamethylene, thus—



(Heller, Ber. 1909, 42, 2736).

The tautomerism of phloroglucinol is (Chem. S. 730).

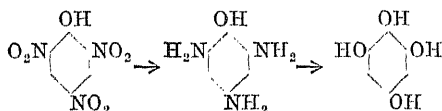
The tetrahydric phenols. There are three theoretically possible tetrahydroxy derivatives of benzene,



all of which have been prepared: two of them occur naturally in the form of their ethers.

1:2:3:4 Tetrahydroxybenzene (Apionol), is the parent *apionols* (v. OILS, ESSENTIAL). It has been prepared synthetically by Einhorn, Coblenger and Pfeiffer (Ber. 1904, 37, 119) by the action of water on the hydrochloride of aminopyrogallol. It forms colourless needles from benzene which melt at 161°. The tetraacetyl-derivative forms needles melting at 136°. The phenol is readily soluble in water, alcohol or ether, and dissolves in alkali forming a pale yellow solution which does not absorb oxygen from the air. The aqueous solution gives an intense blue colour with ferric chloride. A dimethylmethylether,  $\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{CH}_2$  (Apione), melting at 79°, is formed by the oxidation of Petersilien Apiol. Tetramethylapionol  $\text{C}_6\text{H}_2(\text{OCH}_3)_4$ , melting at 89°, has been prepared by Ciamician and Silber (Ber. 1896, 29, 1808); it is probably identical with the ether prepared from the free phenol and dimethyl sulphate, which melts at 83° (cf. Einhorn, Coblenger and Pfeiffer, l.c. 105).

1:2:3:5-Tetrahydroxybenzene (oxyphloroglucinol), is formed from picric acid by reduction and elimination of the amino groups by boiling the hydrochloride of the amino compound with water



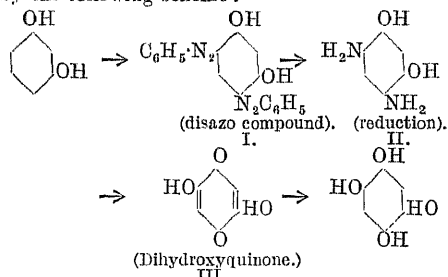
In the first instance, the trihydroxyamino-benzene  $\text{C}_6\text{H}_2(\text{OH})_3\text{NH}_2$ , is formed, but on heating with water at 150° the remaining amino group is eliminated (Will, Ber. 1888, 21, 609, 2020).

The tetrahydric phenol forms slender needles melting at 165°, and the aqueous solution gives a deep-red colour with ferric chloride. The monomethylether (2-methoxy-1:3:5-trihydroxybenzene, *iretol*), is formed by the decomposition of the glucoside *iridine* (from violet roots); it forms white needles which melt at 186° and are readily soluble in water. The trimethyl ether (1:2:3-trimethoxy-5-hydroxybenzene) has been prepared by Graebe and Suter (Annalen, 1905, 340, 222). It melts at 146° and is identical with Kiliani's antiarol. For other derivatives of this phenol, see Bargellini and Bini (Chem. Zentr. 1911, i. 392).

1:2:4:5-Tetrahydroxybenzene, is formed

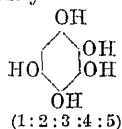


from resorcinol in a manner which is indicated by the following scheme:—

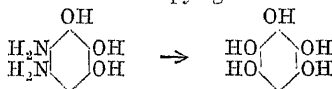


Pentahydroxyphenol (I.) is formed by the action of sodium chloride on resorcinol in the presence of excess of caustic alkali. This is reduced to diaminoresorcinol (II.), which yields diaminoresorcinol on oxidation, a substance which is converted into dihydroxyquinone (III.) on treatment with caustic alkali; the last-named compound is reduced to the tetrahydric phenol by stannous chloride. The tetrahydroxybenzene forms glistening leaflets which melt between 215° and 220°; the aqueous solution becomes rapidly brown on exposure to the air and is at once oxidised to dihydroxyquinone by ferric chloride.

**Pentahydric phenol.** There is only one theoretically possible pentahydroxy derivative of benzene, namely—

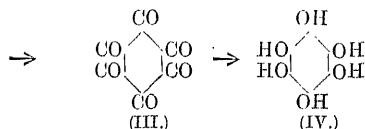
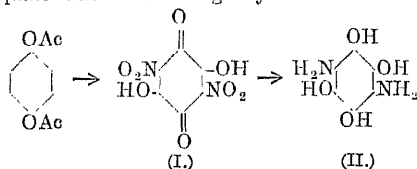


**1:2:3:4:5-Pentahydroxybenzene.** A substance having this constitution has been described by Wenzel and Weidel (Chem. Zentr. 1903 [ii.] 829) as forming colourless crystals insoluble in all the usual organic solvents. Different properties are given to this compound by Einhorn, Coblinger and Pfeiffer (Ber. 1904, 37, 122), who prepared it by the action of water on the hydrochloride of 4:6-diaminopyrogallol



It forms microscopic needles when crystallised from benzene which are readily soluble in ether, alcohol, or ethyl acetate, and which blacken when heated. The pentacetyl derivative forms colourless needles which melt with decomposition at 165°.

The only *hexahydric phenol*, hexahydroxybenzene  $\text{C}_6(\text{OH})_6$ , has been prepared by Nietzki and Benekiser (Ber. 1885, 18, 499, 1833) from the diacetyl derivative of hydroquinone in the following way—



The diacetyl derivative is converted into the triquinoyl derivative (I.) by the action of nitric and sulphuric acids; this is then reduced to diaminotetrahydroxybenzene (II.), which is oxidised by means of nitric acid to triquinoyl (III.); the latter is then reduced by stannous chloride to hexahydroxybenzene (IV.). The hexahydric phenol forms long needles which cannot be obtained completely colourless; when heated it becomes dark-grey at about 200° without melting. It is sparingly soluble in cold water, but readily dissolves on warming, and is sparingly soluble in alcohol, ether, or benzene. The aqueous solution becomes quickly red-violet on exposure to the air and at once reduces silver nitrate. It is oxidised by concentrated nitric acid to triquinoyl and when its alkaline solution is treated with air, it is converted into tetrahydroxyquinone. The action of dilute alkali yields potassium croconate, and acetic anhydride produces the *hexahydroxybenzene* derivative which melts at 203° (Magenheimer, Bull. Soc. chim. 1887, 48, 64). The potassium salt of hexahydroxybenzene is identical with 'kohlenoxydkalium,' which is prepared by the action of dry carbon monoxide on melted potassium (Gmelin, Pogg. Ann. 1825, 4, 35). J. F. T.

#### PHENOL COLOURING MATTERS v. OXAZINE COLOURING MATTERS.

##### PHENOL CORALLIN v. AURIN.

#### PHENOLPHTHALEIN v. TRIPHENYLMETHANE COLOURING MATTERS.

##### PHENOPHENANTHRAZINE v. AZINES.

##### PHENOSAFRANINE v. AZINES.

##### PHENOSAL v. SYNTHETIC DRUGS.

##### PHENYFORM v. SYNTHETIC DRUGS.

**PHENYL.** Under this heading will be described the monosubstituted derivatives of benzene, having the general formula  $\text{C}_6\text{H}_5\text{R}$ . The radicle  $\text{C}_6\text{H}_5$  is known as phenyl and is monovalent.

##### Aminobenzene v. ANILINE.

**Bromobenzene, Phenylbromide**  $\text{C}_6\text{H}_5\text{Br}$ . Prepared by the interaction of benzene and bromine in the presence of sunlight (Schramm, Ber. 1885, 18, 608), iodine (Rilliet and Ador, *ibid.* 1875, 8, 1287), aluminium chloride (Leroy, Bull. Soc. chim. 1887, 48, 211; Greene, Compt. rend. 90, 40), or aluminium amalgam (Cohen and Dakin, Chem. Soc. Trans. 1899, 894); by the action of phenylhydrazine on perbromacetone (Levy and Jedlicka, Annalen, 249, 84); by the action of sulphur bromide and nitric acid on benzene (Edinger and Goldberg, Ber. 1900, 33, 2384); by diazotising aniline in the presence of copper, sulphuric acid, and potassium bromide (Sandmeyer, *ibid.* 1884, 17, 2650); for electrolytic method v. Votoček and Zenišk (Chem. Zentr. 1899, i. 1146).

Bromobenzene is a colourless liquid, b.p. 156.6° (758.6 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 70); m.p. -30.5° (corr.) (Schneider, *ibid.* 22, 232; cf. Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1.5105, 15°/15° 1.4991, 25°/25° 1.4886, 50°/50° 1.4681, 100°/100° 1.4416; magnetic

rotation (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Ramsay and Young, *ibid.* 1885, 646, 655; Young, *ibid.* 1889, 488, 506; Kahlbaum, Zeitsch. physikal. Chem. 26, 584); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 386). Heated with aluminium chloride, bromobenzene yields benzene and isomeric dibromobenzenes (Dunreicher, Ber. 1882, 15, 1867); with sodium methoxide at 200° anisole, phenol, and a small quantity of benzene are formed (Blau, Monatsh. 7, 626). Sodium in ether yields hydrocarbons of high molecular weight and a dark-blue substance (Weiler, Ber. 1896, 29, 115; Mohr, J. pr. Chem. 1909, [ii.] 80, 315); ethyl oxalate and sodium in absolute ether yield benzoic acid and 'phenyl-carbinol' (Frey, Ber. 1895, 28, 2315). Heated with sulphuric acid, bromobenzene yields 1:3:5-dibromobenzene sulphonic acid and a bromobenzene disulphonic acid (Herzig, Monatsh. 2, 192); nitric acid (sp.gr. 1.5) gives 1:2:4-bromodinitrobenzene together with *o*- and *p*-bromonitrobenzenes (Bandrowski, Bull. Acad. Sci. Cracow, 1900, 193). Hydriodic acid and phosphorus are without action on bromobenzene at 218° (Klages and Liecke, J. pr. Chem. [ii.] 61, 319).

**Chlorobenzene, Phenyl chloride,  $C_6H_5Cl$ .** Prepared by the action of phosphorus pentachloride on phenol (Lévy, Compt. rend. 1890, 109; Laurent, Annalen, 75, 79); by heating benzene with thionyl chloride at 150° (Dubois, Zeitsch. Chem. 1866, 705) or with sulphur chloride at 250° (Schmidt, Ber. 1878, 11, 1173); by the electrolysis of a strong hydrochloric acid solution of cupric chloride in the presence of benzene diazonium chloride using copper electrodes (Votoček and Zeníšek, Chem. Zentr. 1899, i. 1146; cf. Walter, J. pr. Chem. 1896, [ii.] 53, 427); by diazotising aniline and heating the product with cuprous chloride (Sandmeyer, Ber. 1884, 17, 1633); by the action of chlorine on benzene in the presence of aluminium chloride (Mouneyrat and Pouret, Compt. rend. 1898, 127, 1026), ferric chloride (Thomas, *ibid.* 1898, 126, 1212), or a mixture of finely divided iron and ferric chloride (D. R. P. 219242; J. Soc. Chem. Ind. 1910, 619).

Chlorobenzene is a colourless liquid, b.p. 131.8° (757 mm.) (Perkin, Chem. Soc. Trans. 1896, 387; cf. Ramsay and Young, *ibid.* 1885, 642, 654; Fuchs, Zeitsch. angew. Chem. 1898, 869); m.p. -45° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 155); sp.gr. 4°/4° 1.1230, 15°/15° 1.1125, 25°/25° 1.1042, 50°/50° 1.0868, 100°/100° 1.0623 (Perkin, *loc.*); critical temperature 359.2° (Young, Zeitsch. physikal. Chem. 11, 590; Schneider, *ibid.* 70, 626); vapour pressure (Young, Chem. Soc. Trans. 1889, 90, *et seq.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); magnetic rotation (Perkin, *loc.*); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 387). By passing the vapour of chlorobenzene over red-hot iron filings, diphenyl, mono- and di-chlorodiphenyl and chlorobenzene are formed (Kramers, Annalen, 180, 135). On heating with sodium in carbon tetrachloride, chlorobenzene, hexaphenylbenzene and

(Schmidlin, Compt. rend. 1903, 137, 59), whilst with aluminium chloride the products are the chlorides of 4:4'- and 2:4'-dichlorobenzophenones (Norris and Green, Amer. Chem. J. 1901, 26, 492; Norris and Tweig, *ibid.* 1903, 30, 392). Chlorine in the sunlight yields  $C_6H_5ClCl_4$ ,  $C_6H_4Cl_2Cl_3$ , and other products; in the presence of dilute sodium hydroxide,  $\alpha$ - and  $\beta$ -chlorobenzene hexachlorides are produced (Matthews, Chem. Soc. Trans. 1891, 167; 1892, 103). Bromine in the presence of aluminium chloride yields *p*-chlorobromobenzene and other products (Mouneyrat and Pouret, Compt. rend. 1899, 129, 605); sulphuric acid and iodine yield chlorodiodobenzene ( $Cl:I_2=1:2:4$ ), chlorotriiodobenzene ( $Cl:I_3=1:2:4:6$ ) and other products (Istrati, Chem. Zentr. 1897, i. 1161). Chlorobenzene remains unchanged on heating with hydriodic acid and phosphorus at 302° (Klages and Liecke, J. pr. Chem. [ii.] 61, 319). Nitric acid at 0° gives *o*-, *m*-, and *p*-chloronitrobenzenes, the yields being 29.8, 0.3 and 69.9 p.c. respectively (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1905, 7, 266). Oxidised by sulphuric acid and manganese dioxide to formic and *p*-chlorobenzoic acids. Has been recommended as a solvent for resins (Andès, Chem. Rev. Fett. Harz-Ind. 1906, 13, 32). For stability of chlorobenzene v. Löwenherz (Zeitsch. physikal. Chem. 1899, 29, 401); Vandeveldt (Chem. Zentr. 1898, i. 438).

**Iodobenzene, Phenyl iodide,  $C_6H_5I$ .** Prepared by the action of phosphorus triiodide on phenol (Scrugham, Annalen, 92, 318); by heating a mixture of benzene and iodine with aluminium chloride (Green, Compt. rend. 90, 40), ferric chloride (Meyer, Annalen, 231, 195), or with phosphorus pentachloride (Neumann, *ibid.* 241, 84; Istrati, *loc. cit.* Chem. Zentr. 1892, i. 625), in the last method higher halogenated compounds also being formed; by the interaction of benzene and sulphur iodide in the presence of nitric acid (Edinger and Goldberg, Ber. 1900, 33, 2876); by heating phenyl hydrazine with excess of iodine in potassium iodide solution (Meyer, J. pr. Chem. [ii.] 36, 115); by heating benzene with potassium iodate and dilute sulphuric acid (Peltzer, Annalen, 136, 107); by heating sodium benzoate with iodine (Berthelot, Compt. rend. 1861, 340; *ibid.* 1862, 340).

Iodobenzene is a colourless liquid, b.p. 188.36° (755.75 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 71); m.p. -28.5° (corr.) (Schneider, *ibid.* 19, 157; cf. Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1.8551, 15°/15° 1.8401, 25°/25° 1.8283, 50°/50° 1.8067, 100°/100° 1.7832 (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Young, *ibid.* 1889, 490, 510); heat of combustion 770.0 Cal. (Berthelot, Compt. rend. 130, 1098); magnetic rotation (Perkin, *loc.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 2318). Iodobenzene is reduced to benzene by sodium amalgam in alcohol; with aluminium chloride it yields benzene, isomeric diiodobenzenes, hydrochloric acid and iodine (Dunreicher, Ber. 1882, 15, 1868); with silver nitrate at 145° picric acid is formed (Genther, Annalen, 245, 100); oxidised by Caro's acid to tetrachloro-*p*-benzoic acid (Bamberger and Will, Ber. 1900, 33, 2876).

Nitric acid (sp.gr. 1.5) yields *o*- and *p*-nitroiodobenzenes (Körner, Gazz. chim. ital. 4, 305); chlorine in chloroform solution gives a dichloride (Willgerot, J. pr. Chem. [ii.] 33, 155). Iodobenzene is unchanged by heating with hydriodic acid and phosphorus at 182° (Klages and Liecke, *ibid.* 61, 319); action of ferric chloride and ferric bromide *v.* Thomas (Compt. rend. 128, 1577).

#### Nitrobenzene *v.* BENZENE.

**Phenyl azoimide, Triazobenzene, Diazobenzeneimide**  $C_6H_5N_3$ . Prepared by the action of ammonia (Greiss, Annalen, 137, 68) or of phenylhydrazine (Oddo, Gazz. chim. ital. 20, 798) on diazobenzene perbromide; by the action of nitrous acid on phenylhydrazine at 0° (Dimroth, Ber. 1902, 35, 1032); by passing nitrosyl chloride into a solution of phenylhydrazine in glacial acetic acid (Tilden and Millar, Chem. Soc. Trans. 1893, 257); by heating nitrosocarbamide with dilute potassium hydrate, Annalen, 190, 92) or with alcoholic hydrochloric acid (O. Fischer, Ber. 1886, 19, 2995); by the interaction of stannous chloride and diazobenzene chloride in hydrochloric acid solution (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 99), or of diazobenzene sulphate and sodium azide or hydrazine (Noelting and Michel, Ber. 1893, 26, 86, 89); by the action of sodium cyanide on phenyl isocyanate (Bamberger, *ibid.* 1902, 35, 8895).

Phenyl azoimide is a pale yellow oil having an aromatic-ammoniacal smell, b.p. 73.5° at 22–24 mm.; sp.gr. 0°/4° 1.2339 (Oddo), 10°/10° 1.0980, 25°/25° 1.0853 (Perkin, Chem. Soc. Trans. 1896, 1245); insoluble in water, soluble in alcohol or ether. Explodes on distillation at atmospheric pressure. On heating with concentrated hydrochloric acid, it decomposes into nitrogen and *o*- and *p*-chloranilines (Greiss, Ber. 1886, 19, 313). Strong sulphuric acid very dilute acid yields triazobenzene (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 97). Reduction in alcoholic solution with sodium amalgam gives hydrazobenzene (Curtius, *ibid.* [ii.] 52, 210), with zinc and hydrochloric acid ammonia and aniline. Hydrazine hydrate yields benzene, ammonia and nitrogen (Curtius and Dedichen, *ibid.* [ii.] 50, 252). Phenyl azoimide yields triazo compounds by condensation with substances containing a reactive methylene group (Dimroth, Ber. 1902, 35, 4041); it reacts with alkyl diazoamines forming diazoamino compounds (Dimroth, *ibid.* 1903, 36, 909).

**Phenyl carbimide, Phenyl isocyanate, Carbanil**  $C_6H_5N=C=S$ . Prepared by distilling oxanilide (Hofmann, Annalen, 74, 33), diphenylurea (J. 1858, 348) or phenylurethane (Ber. 1870, 3, 655) with phosphorus pentoxide; by distilling oxanilide chloride (Asehan, *ibid.* 1890, 23, 1825); by heating phenylthiocarbimide with mercuric oxide (Kühn and Liebert, *ibid.* 1536); by decomposing diazobenzene sulphate with potassium cyanate and copper powder (Gattermann, *ibid.* 1225; 1892, 25, 1086); by passing phos-

gene over fused diphenylurea or better over fused aniline hydrochloride (Hentzel, *ibid.* 1884, 17, 1284; *cf.* D. R. P. 19019; *Frdl.* i. 578).

Phenylcarbimide is a colourless liquid, the vapour of which excites tears; b.p. 166° at 769 mm. (Hofmann, Ber. 1885, 18, 764); sp.gr. 1.092 at 15°. With water it yields diphenylurea, with alcohol phenylurethane, and with ammonia monophenylurea. It is much used as a reagent for detecting the presence of hydroxyl and imino groups: condensation with alcohols (*v.* Hofmann, Annalen, 74, 16; Ber. 1871, 4, 249; Tessmer, *ibid.* 1885, 18, 968; 1886, 19, 2606; Snape, Chem. Soc. Trans. 1885, 770; Gumpert, J. pr. Chem. [ii.] 32, 278; Bloch, Bull. Soc. chim. [iii.] 31, 49, 71); with phenol (*v.* Leuckhart and Schmidt, Ber. 1885, 18, 2338). By heating with dilute hydrochloric acid, ammonium chloride, aniline, and carbon dioxide are produced; with acetic acid, diphenylurea, and traces of aniline and acetanilide (Dieckmann and Kammerer, *ibid.* 1907, 40, 373); with acetic anhydride at 170° acetanilide, benzene and carbon dioxide (Gumpert, J. pr. Chem. [ii.] 31, 121); with potassium acetate at 100° triphenylisocyanurate (Hofmann, Ber. 1885, 18, 765). It combines with prussic acid in benzene after the addition of a few drops of pyridine to form cyanoformanilide (Dieckmann and Kammerer, *ibid.* 1905, 38, 2977), and with hydrogen chloride to give chloroformanilide (Hentzel, *ibid.* 1885, 18, 1178). Heated in sealed tubes at 180° it yields carbonyl chloride (Stollé, *ibid.* 1908, 41, 112); it gives aniline. It combines with two atoms of chlorine or bromine. With benzene in the presence of aluminium chloride it gives benzanilide (Leuckhart, *ibid.* 1885, 18, 873; J. pr. Chem. [ii.] 41, 301).

#### Phenyl cyanide, benzonitrile *v.* NITRILES.

#### Phenyl isocyanide, Phenylcarbylamine *v.* NITRILES.

#### Phenylhydroxylamine *v.* HYDROXYLAMINE.

**Phenylthiocarbimide, Phenyl isothiocyanate, Phenyl mustard oil**  $C_6H_5N=C=S$ . Prepared by heating phenyl isocyanide with phosphorus pentoxide (J. 1858, 349), concentrated hydrochloric acid (Weith and Merz, Zeitsch. Chem. 1869, 589), or phosphorus (Hofmann, Ber. 1882, 15, 986), or phosphorus pentoxide (Werner, Chem. Soc. Trans. 1883, 18, 338), or phthalic anhydride (Dunlap, Amer. Chem. J. 1896, 18, 332), in the last method phthalanilic acid also being formed. By heating phenyl isocyanide with sulphur (Weith, Ber. 1873, 6, 211), phenyl thiocarbimide with carbon disulphide (Dixon, Chem. Soc. Trans. 1897, 628) or phenyl carbimide with phosphorus (Michael and Palmer, Amer. Chem. J. 6, 200); by the interaction of phenyl isocyanide and aniline (Rathke, Ber. 1884, 17, 1284); or aniline by heating aniline with iodine (Hofmann, *ibid.* 1861, 14, 111; J. Russ. Phys. Chem. Soc. 10, 184).

Phenylthiocarbimide is an unpleasant smelling liquid, b.p. 131° at 760 mm.; sp.gr. 4°/4° 1.1477, 15° 1.1314 (Perkin, Chem. Soc. Trans. 1896, 1204). By boiling with water and sulphuretted hydrogen and carbon disulphide produced (Bamberger,

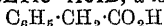
Ber. 1881, 14, 2462); glacial acetic acid at 130° yields acetanilide, carbon oxysulphide, and diphenylurea (Werner, Chem. Soc. Trans. 1891, 548; Claus and Völzow, Ber. 1881, 14, 445; Gumpert, J. pr. Chem. [ii.] 32, 294; Cain and Cohen, Chem. Soc. Trans. 1891, 327); whilst with thioacetic acid it gives acetanilide. It combines with ammonia and substituted amines yielding substituted thioureas. Chlorine forms an addition product; copper powder at 200° yields benzonitrile. Reduction with hydrochloric acid in absolute alcohol gives aniline and thioacetanilide (Pinner, Ber. 1881, 14, 1083), amalgam in neutral solution

gives thioacetanilide and methyl mercaptan (Gutbiere, Ber. 1881, 14, 2033). Sulphuric acid gives carbon disulphide and thioacetanilide (Proskauer and Sell, *ibid.*, 1881, 14, 2033); malonic acid yields diphenylurea and acetanilide, succinic acid succinanil, and sebacic acid, the dianilide of the acid (Bénédic, Compt. rend. 130, 292). By condensing phenylthiocarbimide with aliphatic monohydroxyalcohols, phenylthiourethanes are produced (Hofmann, Ber. 1870, 3, 772; Orndorff and Wheeler, Amer. Chem. J. 1899, 22, 458), with phenol phenyl- $\psi$ -phenylthiocarbamic acid (Dixon, Chem. Soc. Trans. 1890, 268; Snape, *ibid.* 1896, 98) and with aromatic hydrocarbons and phenol ethers substituted thiourethanes (Dixon, J. pr. Chem. 1899, [ii.] 59, 572). Bromine and alcohol in ethereal solution give a dibromo additive compound and phenylthiocarbimide oxide (Fromm and Heyden, Ber. 1881, 14, 2033; Freund and Bachrach, Annalen, 285, 184; Hantzsch and Wolferkamp, *ibid.* 331, 265).

**Phenylthiocyanate**,  $C_6H_5S:C:N$ . Prepared by the action of thiocyanic acid (Billeter, Ber. 1874, 7, 1753) or of cuprous thiocyanate (Gattermann and Haussknecht, *ibid.* 1890, 23, 739) on diazobenzene sulphate; by passing cyanogen chloride into an alcoholic solution of the lead salt of thiophenol (Billeter, *l.c.*).

It is a colourless liquid having a leek-like smell, b.p. 231° (corr.); sp.gr. 1.155 at 17.5°. Concentrated hydrochloric acid at 180°–200° gives thioacetanilide and carbon dioxide; with phenol gives thioacetanilide.

#### PHENYLACETIC ACID, $\alpha$ -toluic acid



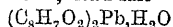
is prepared by the hydrolysis of benzyl cyanide (Cannizzaro, Annalen, 1855, 96, 247; Mann, Ber. 1881, 14, 1645; Stadel, *ibid.* 1886, 19, 1949). It has been obtained by fusing phenylmalonic acid (Wislicenus, *ibid.* 1894, 27, 1094); by boiling vulpic acid with baryta (Möller and Strecker, Annalen, 1860, 113, 64); by fusing atropic acid with potassium hydroxide (Kraut, *ibid.* 1868, 148, 242); by reducing mandelic acid (Brown, Zeitsch. Chem. 1865, 443); by heating phenylchlorovinyl ethyl ether with alcoholic potassium hydroxide (Nef, Annalen, 1899, 308, 318); and by the action of water on an ethereal solution of magnesium benzyl chloride (Zelinsky, Ber. 1902, 35, 2692). It occurs together with thioacetanilide in the products of certain reactions (Ber. 1879, 12, 649; Zeitsch. physiol. Chem. 1888, 2, 420; 1892, 9, 507), and the two are readily separated

by the fractional crystallisation of the zinc salts (Salkowski, *ibid.* 1892, 10, 150). According to Engler and Löw (Ber. 1893, 26, 1436) the presence of benzenoid hydrocarbons in mineral oil may not be exclusively due to a pyrogenetic process, but may arise from the phenylacetic acid produced by the decay of proteid matter.

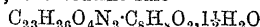
Phenylacetic acid crystallises in thin leaves, m.p. 76.5°, b.p. 265.5° (corr.), 144.2°–144.8°/12 mm. (Anschutz and Berns, Ber. 1887, 20, 1390), sp.gr. 1.0778 at 83°, 1.0334 at 135°/4° (Möller and Strecker, *l.c.*), or 1.228 at 4° (Schröder, Ber. 1879, 12, 1612); the magnetic rotatory power is 12.743 (Perkin, Chem. Soc. Trans. 1896, 1079); and the molecular heat of combustion 933.2 Cal. (Stohmann, Kleber and Langbein, J. pr. Chem. 1889, [ii.] 40, 128). In its physiological action phenylacetic acid differs markedly from phenylpropionic acid which is completely oxidised to benzoic acid when administered as a food to a dog, whilst phenylacetic acid is converted under similar conditions into *phenaceturic acid*  $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , m.p. 143° (E. and H. Salkowski, Ber. 1879, 12, 653). When fed to fowls phenylacetic acid combines with ornithine to produce *phenylaceto-ornithuric acid*

$C_6H_5 \cdot CH_2 \cdot CO \cdot NH(CH_2)_3CH(NH \cdot CO \cdot CH_2 \cdot C_6H_5)CO_2H$  (Totani, Zeitsch. physiol. Chem. 1910, 68, 75).

**Salts.**—Calcium salt  $(C_6H_5O_2)_2Ca \cdot 3H_2O$  (Kraut, *l.c.*); barium salt  $(C_6H_5O_2)_2Ba \cdot 3H_2O$  loses  $2\frac{1}{2}H_2O$  at 150°; lead salt



(Guye, J. 1884, 468); silver salt  $C_6H_5O_2Ag$ ; yttrium salt  $(C_6H_5O_2)_3Y \cdot 3H_2O$  is insoluble (Pratt and James, J. Amer. Chem. Soc. 1911, 33, 1330); the brucine salt



has m.p. 130°–131°,  $[a]_D^{20} = -30.5^\circ$  in 5 p.c., and  $-32.2^\circ$  in  $2\frac{1}{2}$  p.c. chloroform solution (Hilditch, Chem. Soc. Trans. 1908, 1388).

**Esters.**—Methyl ester, b.p. 220°, sp.gr. 1.044 at 16° (Radziszewski, Ber. 1869, 2, 208); chloromethyl ester, b.p. 138°–140°/15 mm. (Descudé, Compt. rend. 1902, 134, 716); ethyl ester, b.p. 227.3°, sp.gr. 1.0555 at 4°/4°; 1.0462 at 15°/15°, or 1.039 at 25°/25° (Perkin, Chem. Soc. Trans. 1896, 69, 1238); propyl ester, b.p. 238°, sp.gr. 1.0142 at 18° (Hodgkinson, *ibid.* 1880, 34, 483); isobutyl ester, b.p. 247° (Hodgkinson, *l.c.*); active amyl ester, b.p. 265°–266°/722.7 mm., sp.gr. 0.982 at 20°/4°;  $n_D$  1.4872 at 21°;  $[a]_D +3.84^\circ$  at 22° (Guye and Chavanne, Bull. Soc. chim. 1896, [iii.] 15, 292); benzyl ester, b.p. 317°–319°, sp.gr. 1.101 (Slawik, Ber. 1874, 7, 1056), b.p. 270°/160 mm., sp.gr. 1.0938 at 170° (Hodgkinson, *l.c.*); menthyl ester, b.p. 192°–197°/10 mm.; sp.gr. 1.002 at 20°/4°; 0.9400 at 100°/4°;  $[a]_D -68.70^\circ$  at 20° (Tschugaeff, Ber. 1898, 31, 2451; Cohen and Dudley, Chem. Soc. Trans. 1908, 1749); phenyl ester, m.p. 42°, b.p. 158°/17 mm. (Stoermer and Biesenbach, Ber. 1905, 38, 195°);  $n_D$  1.511 at 20°; m.p. 28°, b.p. 330° (*ibid.*, 1900, 33, 1720).

$C_6H_5 \cdot CH_2 \cdot COCl$  has b.p. 95.1°–95.8°/12 mm., 102.5°/17 mm., 104°–105°/23 mm., or 170°/250 mm.; sp.gr. 1.16817 at 20°/4°, 1.856 at 4°/4°, 1.1753 at 11°/16°, 1.1674 at 15°/15°; and yields the *anhydride*,

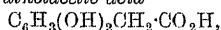
m.p. 72.5°, on heating with oxalic acid (Anschütz and Berns, Ber. 1887, 20, 1389; Schott, *ibid.* 1896, 29, 1986; Perkin, Chem. Soc. Trans. 1896, 69, 1244).

*Phenylacetamide*  $C_6H_5 \cdot CH_2 \cdot CO \cdot NH_2$  has m.p. 154°–155°, b.p. 281°–284° (Weddige, J. pr. Chem. 1873, [ii.] 7, 100); the *diethylamide* has m.p. 86°, b.p. 295°–297° (corr.); the *diphenylamide* has m.p. 72° (Hausknecht, Ber. 1889, 22, 324); the *hydrazide* has m.p. 116°; the *azoimide* is a colourless oil and yields with bromine a crystalline compound, m.p. 121° (Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314). *Phenylaceturonitrile*  $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CN$  has m.p. 90.5°; *ethyl phenylaceturate*, m.p. 82° (Klages and Haack, Ber. 1903, 36, 1646); m.p. 113° (Diels, *ibid.* 1906, 39, 2056).

Phenylacetic acid and the derivatives described above contain a methylene group of similar reactivity to that in malonic acid, ethyl acetoacetate, &c., and they therefore undergo the Claisen condensation (Boeseken, Rec. trav. chim. 1896, 15, 161; Hodgkinson, Chem. Soc. Proc. 1886, 188); form condensation products with aldehydes (Röhmer, Ber. 1898, 31, 281; Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314); react with ethyl nitrate and nitrite (Müller, Ber. 1883, 16, 1617; 2985; Wislicenus and Grützner, *ibid.* 1909, 42, 1930; Noetting and Kadiera, *ibid.* 1906, 39, 2056); and form halogen substituted and amino derivatives that contain an asymmetric carbon atom and have been resolved into their optically active constituents (Easterfield, Chem. Soc. Trans. 1891, 71; Walden, Ber. 1895, 28, 1287; Zeitsch. physikal. Chem. 1895, 17, 705; Bischoff, Ber. 1897, 30, 276; Kossel, *ibid.* 1891, 24, 4145; Stadnikoff, J. Russ. Phys. Chem. Soc. 1906, 38, 943; Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 438; Fischer and Weichhold, Ber. 1908, 41, 1286; Betti and Mayer, *ibid.* 2071).

In addition to the derivatives already described or to which reference has been made, phenylacetic acid forms a series of substituted derivatives in which the substituent has replaced hydrogen of the benzene ring. With the exception of a *dihydroxy* derivative (*homogentisic acid*), the compounds belonging to this series are not of sufficient importance for the purpose of this article to warrant description; and for the preparation and properties of the halogen, nitro and nitro-halogen, &c., derivatives, see Jackson and Lowery, Ber. 1877, 10, 1209; Jackson and Field, Amer. Chem. J. 2, 85; Mabery and Jackson, Ber. 1878, 11, 55; Zincke and Böttcher, Annalen, 1905, 343, 100; Maxwell, Ber. 1879, 12, 1764; Bedson, Chem. Soc. Trans. 1880, 90; Gabriel, Ber. 1881, 14, 2341; 1882, 15, 834, 1992; Gabriel and Meyer, *ibid.* 1881, 14, 823; Gabriel and Borgmann, *ibid.* 1883, 16, 2064; Meyer, Chem. Zentr. 1885, 516; Ber. 1888, 21, 1306; Bedson, *ibid.* 1877, 10, 530, 1657; Jackson and Robinson, Amer. Chem. J. 11, 541; Jackson and Carlton, *ibid.* 1904, 31, 360; Jackson and Shortt Smith, *ibid.* 1904, 32, 168; Reissert, Ber. 1908, 41, 3921; Traube, *ibid.* 1882, 15, 2110; and Traube, *ibid.* 1889, 22, 3207).

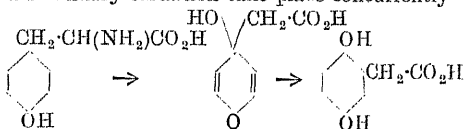
*Homogentisic acid*, 2:5-dihydroxyphenylacetic acid, *guinolacetic acid*



occurs in the urine of certain individuals suffering from *alcaptonuria*, the name *alcapton* being applied by Bödeker (Zeit. rat. Med. 1859, 7, 130) to a reducing substance occurring in certain urines that became brown on addition of alkali in the presence of oxygen (compare also Kirk, Brit. Med. J. 1888, 2, 232; 1889, 2, 1149). The acid was first isolated and identified by Wolkow and Baumann (Zeitsch. physiol. Chem. 1894, 15, 228), and the name *homogentisic acid* applied to it. Homogentisic acid occurs also in the blood serum of alcaptonurics (Abderhalden and Falta, Zeitsch. physiol. Chem. 1903, 39, 143); but the statements that it is found in sugar-beet juice (Gonnermann, Chem. Zeit. 1899, 23, 213) and in seedlings (Bertel, Chem. Zentr. 1903, i. 178) have not been confirmed by later investigations (Schulze, Zeitsch. physiol. Chem. 1907, 50, 508; Schulze and Castoro, *ibid.* 1906, 48, 396).

*Origin of homogentisic acid in the organism.* According to Embden (Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304); Wolkow and Baumann, (*l.c.*); Mittelbach (Chem. Zentr. 1901, ii. 1213); Neubauer and Falta (Zeitsch. physiol. Chem. 1904, 42, 81); Blum (Arch. exp. Path. Pharm. 1908, 59, 273); and Neubauer (Deut. Archiv. Klin. Med. 1909, 95, 211), homogentisic acid is a degradation product of phenylalanine and tyrosine, and in the normal individual it undergoes ultimate oxidation to carbon dioxide and water, but owing to an idiosyncrasy in metabolism the alcaptonuric excretes the acid without further change. Dakin and Wakeman (J. Biol. Chem. 1911, 9, 139, 151), however, maintain that alcaptonuria represents a condition in which the formation of homogentisic acid is abnormal as well as the *normal* is katabolism when formed, for such individuals have not lost their power to katabolise simple derivatives of phenylalanine and tyrosine (e.g. *p*-methoxyphenylalanine or *p*-methoxyphenylalanine) provided their structure is such that the formation of substances of the type of homogentisic acid is excluded.

The mechanism of the change whereby tyrosine is converted into homogentisic acid is somewhat obscure. Friedmann (Beitr. Ch. 1911, 304), Neubauer (Zeitsch. physiol. Chem. 1911, 72, 113), the side chain is first degraded, then a relative change of position of the side chain and the hydroxyl group, and a secondary oxidation take place concurrently



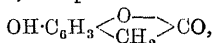
Tyrosine.

Homogentisic acid.

The average excretion of homogentisic acid in cases of alcaptonuria is fairly uniform (Garrod and Hele, J. Physiol. 1905, 33, 198); the amount is, however, increased by the administration of tyrosine or phenylalanine, or of peptides or proteids that yield tyrosine on hydrolysis (Embden, Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304; Falta and Langstein, *ibid.* 1903, 37, 513; Neubauer and Falta, *ibid.* 1904, 42, 81; Abderhalden and Bloch, *ibid.* 1907, 52, 435; 53, 464; Abderhalden, Massini, *ibid.* 1910, 66, 140; Blum, *l.c.*; Neubauer, *l.c.*).

Homogentisic acid has been synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethylchloracetate and aluminium chloride, and . . . . . lysis with red phosphorus and . . . . . acid of the methyl ether of homogentisic acid thus obtained (Osborne, Proc. Physiol. Soc. 1903, 13, 14).

Homogentisic acid forms prisms that melt at 146.5°–147°, and pass into the lactone



m.p. 191°. The lead salt  $\text{Pb}(\text{C}_6\text{H}_3\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$  has m.p. 214°–215°, is soluble in 675 parts of water at 20°, and advantage is taken of this sparing solubility in the isolation of the acid. The ethyl ester has m.p. 119°–120°; the dimethyl ether  $(\text{OMe})_2\text{C}_6\text{H}_3\text{CH}_2\text{CO}_2\text{H}$  has m.p. 124.5°; and its methyl ester  $(\text{OMe})_2\text{C}_6\text{H}_3\text{CH}_2\text{CO}_2\text{Me}$ , m.p. 45° (Wolkow and Baumann, Zeitsch. physiol. Chem. 1894, 15, 228; Baumann and Fränkl, *ibid.* 20, 221). Dibenzoylethylhomogentisamide has m.p. 204° (Orton and Garrod, J. Physiol. 1901, 27, 89). Homogentisic acid reduces copper and silver salts readily, gives a blue colour with ferric chloride, and yields gentisic acid (2:5-dihydroxybenzoic acid) and quinol on fusion with potassium hydroxide at 196°–198°. For the chemistry of the colour reactions afforded by . . . . . acid with amines, see Möerner, . . . . . Chem. 1910, 69, 329.

**Estimation.**—Homogentisic acid in urine is estimated by . . . . . action on silver nitrate. . . . . urine, 10 c.c. of ammonia solution (8 p.c.), 20 c.c. of N/10 silver nitrate solution are placed in a flask, after five minutes 5 drops of calcium chloride and 10 drops of ammonium carbonate solution are added, the solution made up to 50 c.c., and the silver estimated in half the filtrate. One molecule of homogentisic acid reduces 4 atoms of silver (Baumann, Zeitsch. physiol. Chem. 1895, 16, 268; Denigès, J. Pharm. Chem. 1897, [vi.] 5, 50; Gar . . . . . 7. Physiol. 1905, 33, 206).

**PHENYLALANINE.**  $\beta$ -phenyl- $\alpha$ -aminopropionic acid,  $\alpha$ -aminohydrocinnamic acid  
 $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2)\text{CO}_2\text{H}$

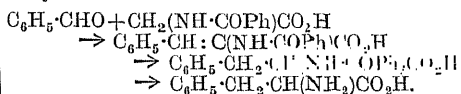
was discovered in the etiolated seedlings of *Lupinus luteus* (Schulze and Barbieri, Ber. 1879, 12, 1924; 1881, 14, 1785), and occurs in many other germinating plants (Schulze, Zeitsch. physiol. Chem. 1888, 12, 405; 1892, 17, 193; 1894, 20, 306; 1896, 22, 411; 1900, 30, 241). Winterstein (*ibid.* 1904, 41, 485) found it among other products of proteid hydrolysis in Emmen-thaler cheese; and Abderhalden and Barker (*ibid.* 1904, 42, 524) showed that it occurs in the urine of dogs suffering from pho . . . . .

The naturally occurring . . . . . originates from the protein of . . . . . plant, and it can also be . . . . . by the hydrolysis of a large number of proteids (v. PROTEINS) by means of hydrochloric acid, stannous chloride, or baryta (Schulze and Barbieri, Ber. 1883, 16, 1711; Zeitsch. physiol. Chem. 1884, 9, 63); it occurs in that fraction of the esterified products of hydrolysis that boils at 130°–160°/0.5 mm., and is isolated by precipitation from the mixed esters by means of water (Fischer, *ibid.* 1901, 33, 412),

or by means of its sparingly soluble copper salt (Schulze and Barbieri, J. pr. Chem. 1883, [ii.] 27, 337; compare Schulze and Winterstein, Ber. 1902, 35, 210).

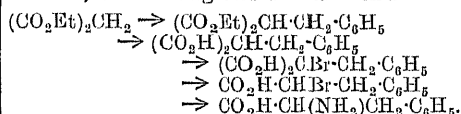
**Synthesis.**—The constitution of phenylalanine was determined by Erlenmeyer and Lipp (Ber. 1882, 15, 1006), who synthesised it from phenylacetaldehyde, hydrogen cyanide, and ammonia  
 $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CHO} \rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2)\text{CN}$   
 $\rightarrow \text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2)\text{CO}_2\text{H}.$

Plöchl (*ibid.* 1883, 16, 2815; 1884, 17, 1616) obtained it by the reduction and subsequent hydrolysis of . . . . . acid obtained by the . . . . . aldehyde with hippuric acid in the presence of acetic anhydride—



For a complete explanation of the mechanism of this reaction which is more complex than indicated above, see Erlenmeyer (Annalen, 1893, 275, 1, 13); and Erlenmeyer and Kunlin (*ibid.* 1899, 307, 146).

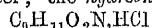
For the preparation of synthetic phenylalanine Fischer's method is the most practical (Ber. 1904, 37, 3062). It consists in the preparation of the corresponding bromo-fatty acid starting with ethyl malonate and benzyl chloride, and treating this with ammonia—



For other methods of synthesis, see Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); Wheeler and Hoffman (Amer. Chem. J. 1911, 45, 368).

The phenylalanine obtained by any of the synthetic processes described above is the racemic (*dl*-) form, it can be resolved into its optically active isomerides by the fractional crystallisation of the cinchonine salt of the benzoyl derivative (Fischer and Mouneyrat, Ber. 1900, 33, 2383), or the brucine salt of the formyl derivative (Fischer and Schoeller, Annalen, 1907, 357, 1). *d*-Phenylalanine can be obtained by the selective action of yeast in a sucrose solution on . . . . . (Ehrlich, Biochem. Zeitsch. 190 . . . . .)

***l*-Phenylalanine** crystallises in anhydrous shining plates or hydrated needles containing 4 p.c. water (Schulze and Winterstein, *l.c.*), soluble in 32.4 parts of water at 25°, m.p. 278° (corr.) with decomposition,  $[\alpha]_D^{20} - 35.1^\circ$ , and has a slightly bitter taste (Fischer and Schoeller, *l.c.*). The copper salt  $(\text{C}_6\text{H}_9\text{O}_2\text{N})_2\text{Cu}$  is almost insoluble in water; the hydrochloride



and hydrobromide are crystalline and stable; the ethyl ester  $\text{C}_8\text{H}_9\text{N} \cdot \text{CO}_2\text{Et}$  is an oil and forms a crystalline hydrochloride  $\text{C}_8\text{H}_9\text{N} \cdot \text{CO}_2\text{Et} \cdot \text{HCl}$ ,  $[\alpha]_D^{20} - 7.6^\circ$ ; the formyl derivative forms sharp four-sided plates, m.p. 167° (corr.), and has  $[\alpha]_D^{20} + 75.2^\circ$ ; the brucine salt crystallises in warty masses from methyl alcohol; the benzoyl

derivative is more readily soluble than that of the racemic form, and has not been obtained pure (Schoeller, l.c.).

In the normal individual phenylalanine is completely destroyed in the system, and when administered as a food it causes no increase in the amount of aromatic substances in the urine; in certain abnormal cases (*alcaptonuria*) the phenylalanine is not completely oxidised in the system and is excreted in the form of *phenylpyruvic acid* (v. PHENYLACETIC ACID).

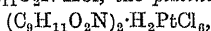
*Phenylalanine* (corr.), with decomposition;  $[\alpha]_D^{20} +35.08$  in 2 p.c. aqueous solution;  $[\alpha]_D^{20} +7.07$  in 3.5 p.c. solution of 18 p.c. hydrochloric acid (Fischer and Mouneyrat, l.c.); and has a sweet taste. The *hydrobromide* forms silky needles, the *formyl* derivative  $C_{10}H_{11}O_3N$  crystallises in needles or plates  $[\alpha]_D^{20} -75.43$ , soluble in 145 parts of water at 27°, and melts at 167° (corr.); the *benzoyl* derivative  $C_{16}H_{15}O_3N$  forms colourless needles, m.p. 145°–146° (corr.),  $[\alpha]_D^{20} -17.1$  in 7 p.c. N/1 alkali solution, the *cinchonine salt* melts at 180°–181°; the *phenylisocyanate*  $C_{16}H_{15}O_3N_2$  has m.p. 180°–181° (corr.),  $[\alpha]_D^{20} +61.27$  in 8 p.c. alkali solution; the *α-naphthylisocyanate*  $C_{20}H_{15}O_3N_2$  has m.p. 150°–151° (Neuberg and Rosenberg, Biochem. Zeitsch. 1907, 5, 458).

*dl-Phenylalanine* crystallises from water in short stunted prisms, from alcohol in shining plates, difficultly soluble in cold water; it melts at 263°–265° with decomposition (Erlenmeyer and Lipp, l.c.), or at 271°–273° (Sörensen, l.c.). The acidic dissociation constant is  $2.5 \times 10^{-9}$  and the basic dissociation constant is  $1.3 \times 10^{-12}$  (Kanitz, Pflüger's Archiv. 1907, 118, 537). The behaviour of phenylalanine on heating is characteristic, a small quantity sublimes unchanged (1.5 grms. yielded 0.06 gm. sublimate after 2½ hours at 200°/1.5–2 mm., Dakin, J. Biol. Chem. 1909, 6, 235), the remainder decomposes with evolution of carbon dioxide and water and formation of a residue of *phenyl-lactimide* (v. *infra*), and a distillate of *phenyl-ethylamine* (Schulze and Barbieri, l.c.; Erlenmeyer and Lipp, l.c.). On oxidation with chromic acid mixture phenylalanine yields phenylacetaldehyde and finally benzoic acid.

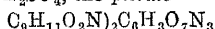
In its physiological action *dl-phenylalanine* resembles the *l*-form, being completely oxidised in the organism of the normal individual, and converted into *l*-phenylalanine in the cases of

conversion of racemic phenylalanine is less complete than that of the *l*-form (Falta and Langstein, Zeitsch. physiol. Chem. 1903, 37, 513). After intravenous or subcutaneous injection of *dl-phenylalanine* in cats or dogs, a large amount is excreted unchanged, and part is converted into *d*-carbamido-phenylpyruvic acid (Dakin, J. biol. Chem. 1907, 5, 458).

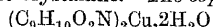
*Derivatives of dl-phenylalanine.* The *hydrochloride*  $C_9H_{11}O_3N \cdot HCl$ , the *platinichloride*



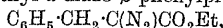
the *nitrate*  $C_9H_{11}O_3N \cdot HNO_3$ , the *sulphate*  $(C_9H_{11}O_3N)_2 \cdot H_2SO_4$ , the *picrate*



m.p. 173°, and *picrolonate*  $C_9H_{11}O_3N \cdot C_{10}H_8O_5N_4$ , m.p. 238°, are crystalline. The *copper salt*

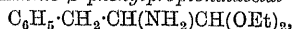


is sparingly soluble in cold water, and becomes anhydrous over sulphuric acid; the *silver salt*  $C_9H_{11}O_3NAg$  is sparingly soluble. The *ethyl ester*  $C_9H_{10}N \cdot CO_2Et$  is a thick oil sparingly soluble in water, b.p. 143°/10 mm., sp.gr. 1.065 at 15°, forms a crystalline *picrate*, m.p. 156.5° (corr.), *hydrochloride*  $C_9H_{10}N \cdot CO_2Et \cdot HCl$ , m.p. 127°, *nitrite*  $C_9H_{10}N \cdot CO_2Et \cdot HNO_2$ , and a *diazo derivative* (ethyl *α*-diazo-*β*-phenylpropionate)

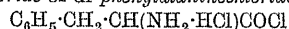


a golden-yellow oil, b.p. 90°–94°/11 mm., sp.gr. 1.107 at 10°/4°,  $n_D^{20} 1.5367$  at 16° (Curtius and Müller, Ber. 1904, 37, 1261). The *methyl ester*  $C_9H_{10}N \cdot CO_2Me$  has b.p. 141°/12 mm., sp.gr. 1.096 at 22°/4°,  $n_D^{20} 1.5203$  at 20°; the *hydrochloride* has m.p. 158°; the *diazo derivative*  $C_6H_5 \cdot CH_2 \cdot C(N_2)CO_2Me$ , bright orange-coloured liquid, b.p. 85°–87°/12 mm., sp.gr. 1.126 at 20°/4°,  $n_D^{20} 1.5435$  at 26° (Curtius and Müller, l.c.).

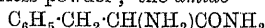
*dl-α-Amino-β-phenylpropionalacetal*



obtained by reducing the ethyl ester, has b.p. 103°–105° (corr.), 0.25 mm. or 153.5°/11 mm., sp.gr. 0.995 at 20°;  $n_D^{20} 1.49383$  (Fischer and Kametaka, Annalen, 1909, 365, 7). The *hydrochloride* of *dl-phenylalanine* *chloride*

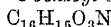


is a colourless powder; the *amide*



has m.p. 138°–140° (corr.), and yields the *β-naphthalenesulphonyl* derivative  $C_{19}H_{15}O_3N_2S_2$ , m.p. 164°–166° (corr.), and *carbethoxy-dl-phenylalanine*, m.p. 141° (corr.) (Koenigs

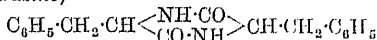
308, 41, 4427). *Formyl-dl-phenylalanine* is soluble in 240 parts of benzoyl derivative



has m.p. 187°–188° (corr.) (Fischer and Mouneyrat), its *methyl ester*  $C_{16}H_{14}O_3N \cdot CH_3$  melts at 87° (corr.), and its *ethyl ester* at 95° (corr.), the *acid chloride*  $C_{15}H_{14}ON \cdot COCl$  has m.p. 123°–125° (corr.) (Max, Annalen, 1907, 365, 7).

*Amide*  $C_{15}H_{14}ON \cdot NH_2$  (Max, Annalen, 1907, 365, 7).

*Phenylalanine*  $C_9H_5 \cdot CH_2 \cdot CH(NH \cdot CO \cdot CH_2Ph)CO_2H$ , m.p. 126° (Erlenmeyer and Kunlin, l.c.). *Phenyl-lactimide* (3 : 6 - *dibenzyl* - 2 : 5 - *diketo* - *piperazine*)



has m.p. 300° (corr.) (Erlenmeyer and Lipp, l.c.; Curtius and Müller, l.c.).

*Phenylisocyanate* of *dl-phenylalanine* has m.p. 182° (with decomp.); the *methylisocyanate* has m.p. 176°–177°,  $[\alpha]_D^{20} -14.0$ ° (Vallée, Ann. Chim. Phys. 1908, [viii.] 15, 331).

For a description of the properties of the chloro, bromo, amino substituted derivatives of phenylalanine in which the substituent is in the benzene ring, see Wheeler and Clapp, Amer. Chem. J. 1908, 40, 337, 458; Abderhalden and Brossa, Ber. 1909, 42, 3411; Erlenmeyer and Lipp, l.c.;

Friedmann and Maase, *Biochem. Zeitsch.* 1910, 27, 97; Flatow, *Zeitsch. physiol. Chem.* 1910, 64, 367. Numerous *polypeptides* containing the phenylalanyl radicle are described by Leuchs and Suzuki (Ber. 1904, 37, 3306); Curtius and Müller (J. pr. Chem. 1904, [ii.] 70, 223); Fischer (Ber. 1904, 37, 3062); Fischer and Blank (Annalen, 1907, 354, 1); Fischer and Schoeller (*ibid.* 1907, 357, 1); Abderhalden and Brossa (Ber. 1909, 42, 3411). M. A. W.

**PHENYLBENZYLHYDRAZINE** *v.* HYDRAZINES.

**PHENYLENE BLUE** *v.* INDAMINES AND INDOPHENOLS.

**PHENYLENE BROWN** *v.* AZO-COLOURING MATTERS.

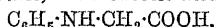
**PHENYLENE DIAMINES** *v.* DIAMINES.

**o-PHENYLENE DIAZO SULPHIDE** *v.* DIAZO COMPOUNDS.

**PHENYLENE VIOLET** *v.* INDAMINES AND INDOPHENOLS.

**PHENYLGLYCINE.** This compound and certain of its derivatives are of great importance, and its nitrile, and its nitrile, have during the last two decades assumed great technical importance, owing to the fact that they are all intermediate products in the manufacture of indigo by one or other of the processes based on the original synthetic method of Heumann (*cf.* INDIGO, ARTIFICIAL).

**Phenylglycine, anilidoacetic acid,**



may be obtained by the action of aniline on chloroacetic or bromoacetic acid (Hausdörfer, Ber. 1899, 22, 1799). The yields, however, are bad, owing to the fact that there is a tendency for two molecules of acid to condense with one of aniline. To avoid this a salt or ester of chloroacetic acid may be employed; various other processes have also been suggested.

#### *Technical methods of preparation.*

(1) Aniline is made to condense with an alkali or alkaline earth salt of chloroacetic acid (Friswell, Eng. Pat. 18149, 1907; D. R. P. 177491). The condensation is brought about in the presence of hydrated ferrous oxide or carbonate (Höchstler Farb. D. R. P. 167698). An ingenious modification of this process is to heat an aqueous solution of chloroacetic acid with nitro-benzene in the presence of finely divided iron, which first brings about the reduction of the nitro-benzene and then forms the insoluble iron salt of phenylglycine. In actual practice it is found advisable to add a small quantity of aniline to start the reaction, which takes place at 100°. When the change is complete, the mixture is distilled with steam to remove the unchanged aniline, and excess of sodium carbonate is added. The solution of the sodium salt of phenylglycine is then filtered and the phenylglycine is obtained by the addition of sulphuric acid (D. R. P. 115797; Eng. Pat. 9700, 1906).

or of the resulting amyl ester is then saponified (Leppmann, D. R. P. 163515).

(2) Phenylglycine may also be prepared by the reduction of oxanilic acid,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{COOH}$

which may be obtained in good yields by heating aniline with excess of oxalic acid. Two methods have been proposed (1) by reduction with sodium amalgam or with zinc dust (Köpp & Co., D. R. P. 163842); (2) by electrolytic reduction with lead cathodes (Kinzlberger, D. R. P. 163842).

(3) Phenylglycine is obtained in large quantities by the action of prussic acid,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , which may be obtained from aniline in good yields by the action of prussic acid and formaldehyde (D. R. P. 145376).

*Properties and Reactions.* White crystals, m.p. 127°, moderately soluble in water, slightly so in ether, but easily so in the usual organic solvents. It forms soluble alkali salts and a green insoluble copper salt, which is an internal complex. On heating at 140° a molecule of water is lost, forming indoxyl, which on oxidation in the air yields indigo; with fuming sulphuric acid it forms indigo sulphonic acid; with bromine water its aqueous solution gives a precipitate of tribromophenylglycine; with acetic anhydride it forms acetylphenylglycine.

*The conversion of Phenylglycine into Indigo.* The fusion with soda or potash to form indoxyl and the subsequent oxidation of this compound by atmospheric oxygen requires a temperature of over 300°, and the yields of indigo are extremely unsatisfactory; it was this fact which made the original Heumann synthesis commercially impracticable. Various condensing agents have been since proposed, and now sodamide is employed extensively and with considerable technical success, in spite of the expense of the sodamide, in the Höchstler dye works.

Among other substances which have been suggested are sodium oxide mixed with soda (Basler Chemische Fabrik, D. R. P. 165691), and also calcium carbide and magnesium nitride (Höchstler Farb., D. R. P. 166213).

*Derivatives.*—*Phenylglycine methyl ester* (m.p. 48°) and *ethyl ester* (m.p. 58°) from aniline and the corresponding ester of chloroacetic acid (D. R. P. 194884).

*Phenylglycine amide* (m.p. 133°) from aniline and chloroacetamide.

*Phenylglycine nitrile* (m.p. 43°) from aniline and chloroacetonitrile, and also by the action of prussic acid and formaldehyde on aniline (Bender). On saponification it yields phenylglycine quantitatively.

*p-Hydroxyphenylglycine amide*, from chloroacetamide and *p*-aminophenol, is employed as a photographic developer (D. R. P. 166790).

*Nitro derivatives of phenylglycine* are described by Deutsch (J. pr. Chem. 1907, [ii.] 76, 350); Borsche and Titsingh (Ber. 1907, 40, 5016); Reverdin (*ibid.* 1909, 42, 4115); Abderhalden and Blumberg (Zeitsch. physiol. Chem. 1910, 65, 318).

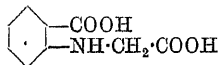
*Phenylglycine-o-sulphonic acid*, obtained by the action of formaldehyde and hydrogen cyanide on aniline (Bradshaw, Amer. Chem. Soc. 1909, 31, 111).

For a number of other derivatives of phenylglycine see Mauthner and Suida (Monatsh. 1890, 11, 380); Widman (Ber. 1896, 29, 1946); Fischer (*ibid.* 1899, 32, 247); Vorländer and Weissbrenner (*ibid.* 1900, 33, 555, 556); Kahn



and Heimann (*ibid.* 1902, 35, 576); Schulz and Jockheim (*ibid.* 1908, 41, 3790); Leuchs and Geiger (*ibid.* 1721); Rupe and Všečoha (Annalen, 1898, 301, 75); Rupe, Heberlien and Roesler (*ibid.* 79); Fischer and Schmidlin (*ibid.* 1905, 340, 190); Pickard (Chem. Soc. Trans. 1902, 1574); de Mulpied (*ibid.* 1905, 438); Lumière and Barbier (Bull. Soc. Chim. 1906, [iii.] 38, 123); Eng. Pat. 5763, 1900.

#### Phenylglycine-*o*-carboxylic acid



is an important intermediate product in the manufacture of indigo. It is obtained by the condensation of anthranilic acid and chloroacetic acid; as, in the case of phenylglycine, the yields are bad, but on working with the sodium salts in aqueous solution at a temperature of 40°, the reaction proceeds smoothly owing to the fact that the sodium salt of the acid crystallises out and is thus protected from further action. Various other methods have been suggested for the preparation of phenylglycine: by heating anthranilic acid with carbohydrates such as starch or mannite or with glycerol (Badische Anilin und Soda Fabrik, D. R. P. 111067); by heating glycine with *o*-chlorobenzoic acid in the presence of copper salts, which act as catalysts (Cie. Paris. Coul. d'Anilin, Fr. Pat. 306302); by the formation and subsequent saponification of  $\omega$ -cyanomethylantranilic acid (exonitrile of phenylglycine); by the action of formaldehyde and prussic acid on anthranilic acid (*cf.* phenylglycine nitrile). This method is used the subject of various patents (D. R. P. 117924; Badische Anilin und Soda Fabrik, D. R. P. 216748).

**Properties and Reactions.** White crystals, m.p. 215° (decomp.); soluble in hot water, alcohol, ether, or acetic acid, but almost insoluble in benzene or chloroform. On heating with water it loses carbon dioxide and forms phenylglycine; on fusion with alkalis it first gives the salt of indoxylcarboxylic acid and then indoxyl, which in the presence of air is oxidised to indigo (Badische Anilin und Soda Fabrik, D. R. P. 111067); on heating with sodium acetate and acetic anhydride it forms diacetyl indoxyl (Bayer and Co., D. R. P. 85071); with fuming sulphuric acid it forms indigosulphonic acids.

**Derivatives.**—Phenylglycine-*o*-carboxylic acid being a dibasic acid, forms two series of mono esters, two nitriles, &c.

**Dimethyl and diethyl esters**, from the esters of chloroacetic acid and anthranilic acid (Höcherster Farbw. D. R. P. 111911); also from the acid itself and alcohol (D. R. P. 120138).

**Exonitrile** (*v.* above).—Its acetyl derivative is obtained by the oxidation of acetyl-*o*-tolylglycine (Bayer and Co., D. R. P. 102892).

**Halogen derivatives** of phenylglycine-*o*-carboxylic acid are readily obtained by the action of halogens on the acid suspended in glacial acetic acid (D. R. PP. 148615, 158089, 216266).

**Nitro derivatives** of the acid are described by P. (Gazz. chim. ital. 1903, 33, [i.] 337) (Monatsh. 1905, 26, 1253).

**Nitroso derivatives**, which are also used in the production of indigo, have been prepared by Vorländer (Ber. 1901, 34, 164; D. R. P. 127577).

Some other derivative of the acid and esters are described in D. R. PP. 138207, 141698, 147633; also by Lumière and Perrin (Bull. Soc. Chim. 1903, [iii.] 30, 966); Villiger (Ber. 1909, 42, 3541); also by Vorländer and Mumme (Ber. 1902, 35, 1699; D. R. PP. 216748; 220839).

#### PHENYLHYDRAZINE *v.* HYDRAZINES.

#### PHENYLHYDRAZINE ACETYL *v.* PYRODINE.

#### PHENYLHYDRAZINE-*p*-SULPHONIC ACID

#### *v.* HYDRAZINES.

#### PHENYLHYDRAZONES *v.* HYDRAZONES.

#### PHENYL HYDROGEN SULPHATE *v.*

#### PHENOL AND ITS HOMOLOGUES.

#### PHENYL-ORTHO-OXALATE *v.* AURIN.

#### PHENYLOSAZONES *v.* HYDRAZONES.

#### PHENYLPARACONIC ACID *v.* LACTONES.

**PHESIN.** A sulpho derivative of phenacetin  $C_6H_5(O \cdot C_2H_5)(SO_2Na)(NH \cdot CO \cdot CH_3)$  used as an antipyretic. Is a light-brown amorphous powder, soluble in water, giving a Bismarck brown solution (*v.* SYNTHETIC DRUGS).

#### PHILADELPHIA YELLOW *G* *Chrysamine* *v.* ACRIDINE DYES.

#### PHLOGOPITE *v.* MICA.

#### PHLORIDZIN *v.* GLUCOSIDES.

#### PHLOROGLUCINOL *v.* PHENOL AND ITS HOMOLOGUES.

**PHLOROL.** The name originally given by Hlasiwetz (Annalen, 1857, 102, 166) to the homologue of phenol obtained by the dry distillation of barium phloretate, and shown by Oliveri (Gazz. chim. ital. 1883, 13, 264) to be identical with *o*-ethylphenol. The term is also applied to the mixture of xylenols that occur with creosol in the fraction of creosote of b.p. 217°–220° (Marasse, Annalen, 1869, 152, 75).

#### PHLOSCEINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

**PHOCNIC ACID.** A name given by Chevreul to isovaleric acid.

#### PHENICITE. *Basic lead chromate* (*v.* CHROMIUM).

**PHENIN** and **PHENICEIN.** Phœnin  $C_{14}H_{16}O_7$ , the glucoside of the leuco compound of phœnicein, is found in the bark parenchyma cells of the *Copaifera bracteata* (Benth.) (purple wood), and crystallises from water in minute colourless needles or rods, which, on standing in air, develop a faintly violet tint. By boiling with methyl alcohol and hydrochloric acid phœnin is converted into phœnicein, and on addition of water to the acid solution is a white powder soluble in ammonia, colouration. Purple wood yields approximately 2 p.c. of phœnicein.

A. G. P.

#### PHENIX POWDER *v.* EXPLOSIVES.

**PHONOLITH.** A mixture of sanidine and nepheline, containing about 9 p.c. of potash. Used as a fertiliser (Krische, Chem. Zeit. 1910, 34, 387).

**PHOSGENE GAS.** J. Davy's name for carbonyl dichloride or carbon oxychloride, *v.* CARBON.

**PHOSGENITE.** A lead chloro-carbonate  $PbCl_2 \cdot PbCO_3$ , *v.* LEAD.

#### PHOSOT *v.* SYNTHETIC DRUGS.

**PHOSPHINE.** A syn. for phosphoretted hydrogen  $PH_3$ , *v.* PHOSPHORUS. Used also to

designate the nitrate of ehrysaniline or diamino-phenylacridine  $C_{19}H_{15}N_3 \cdot HNO_3$ , v. CHRYS-ANILINE.

**PHOSPHOMOLYBDIC ACID** v. MOLYBDE-NUM.

**PHOSPHOR BRONZE** v. TIN.

**PHOSPHORITE** and **ROCK-PHOSPHATE**.

General terms applied to compact or indistinctly crystallised forms of calcium phosphate, of varying degrees of purity, which are often regarded as massive varieties of the mineral apatite (*q.v.*). It is probable, however, that several allied mineral species are represented, and that the material is usually a mixture of these, together with various impurities. The materials are, in fact, more of the nature of rocks rather than simple minerals.

The term phosphorite, first used by R. Kirwan in 1794 as a synonym of apatite, is more properly restricted to the concretionary and stalactitic masses with a mamillated form externally and often a minutely radio-fibrous or convoluted structure internally. Such material, although often containing calcium fluoride in addition to calcium phosphate, differs from crystallised apatite in containing a small proportion of calcium carbonate and water. Phosphorite is generally found filling pockets or veins in limestone; for example, in Estremadura and Quercy; and in the Pacific and West Indian islands it has obviously been formed by the action of phosphatic solutions, leached from guano, on the underlying coral-limestone.

A. Lacroix (Compt. rend. 1910, 150, 1213, 1388; *Minéralogie de la France*, 1910, 4, 555, from a microscopical study of the French phosphorites, separates them from apatite, and places them in a separate division of his classification comprising combinations of phosphates and carbonates. In this division he recognises as species:—

Dahllite,  $2Ca_3(PO_4)_2 \cdot CaCO_3 \cdot \frac{1}{2}H_2O$ .

Francolite (and its fibrous variety staffelite, or 'hydroapatite'),

$(CaF)_2Ca_6(PO_4)_6 \cdot CaCO_3 \cdot H_2O$ .

Collophanite  $x[Ca_3(PO_4)_2] \cdot yCaCO_3 \cdot zH_2O$ .

phanite  $x(CaF)_2Ca_6(PO_4)_6 \cdot yCaCO_3 \cdot zH_2O$ .

The fibres of both dahllite and staffelite are optically uniaxial (or nearly so), with a negative birefringence a little greater than that of apatite.

Collophanite is amorphous, and optically isotropic; and with its vitreous to resinous lustre and conchoidal fracture resembles opal or mother-of-pearl. Only exceptionally, however, do these minerals occur alone in the French phosphorites; as a rule, they form interbanded mixtures, so intimately that a mechanical separation of them is impossible. For this type of mixed phosphorite the name *quercyite* is proposed; quercyite- $\alpha$  when the crystalline element is optically negative, and quercyite- $\beta$  when it is optically positive (the crystalline element in the latter case not corresponding with any known species).

Analyses, by Pisani, are given for these it is seen that the differences in composition are only slight. I. Dahllite from Mouillac, Tarn-et-Garonne. II. Collophanite from Pouzillac, Gard. III. Quercyite- $\alpha$  from Mouillac, Tarn-et-Garonne. IV. Quercy-

ite- $\beta$  from Mouillac. V. Quercyite from Castillo de Belmez, prov. Cordova, Spain.

	I.	II.	III.	IV.	V.
$P_2O_5$	38.40	37.40	37.60	36.60	37.75
CaO	53.65	49.73	51.85	50.45	52.50
F	( <sup>2</sup> )	0.88	1.50	0.83	( <sup>2</sup> )
$CO_2$	5.30	3.75	4.00	4.62	5.70
$H_2O$	2.10	7.05	4.80	6.00	3.20
$Fe_2O_3, Al_2O_3$	0.57	0.50	—	1.30	0.85
	100.02	99.61	99.75	99.80	100.00
Sp.gr.	2.97	2.69- 2.77	2.83- 2.87	—	—

In the French phosphorites occurring as nodules, pebbles, or in sedimentary rocks, or simply as impregnations of phosphatic material in the rocks themselves, the mineralogical identity of the material is still less definite. For details of occurrence and production, see the article FERTILISERS.

Ref.—G. P. Merrill, *The Non-metallic Minerals*, 2nd ed., New York, 1910. O. Stutzer, *Die wichtigsten phosphatischen Nicht-Erze*, 1911, i. *Bibliographie générale des phosphates*, 2nd ed., Annales des Mines, vii., 1902 et seq. F. Wyatt, *The Phosphates of America*, 5th ed., New York, 1894. A. Deckers, *Etude complète sur les phosphates*, Liège, 1894. J. J. H. Teall, *The Natural History of Phosphate Deposits*, Proc. Geol. Assoc. 1900, 16, 369.

L. J. S.

**PHOSPHORUS.** Sym. P. At.w. 31.04. Vapour density = 61.92. From  $\phi\omega\varsigma$ , light; and  $\phi\acute{\epsilon}\rho\omega$ , I bear. Phosphorus was accidentally discovered by an alchemist named Brandt, of Hamburg, while experimenting with urine, in the year 1669. As urine contains only a small quantity of phosphoric acid, phosphorus was not generally known till about 100 years after, when Gahn in 1769 showed it to be an essential constituent of bones, and Scheele, taking advantage of this discovery, made phosphorus from bone ash. It is stated that Brandt by a secret process succeeded in preparing phosphorus from urine, and he is said to have sold the secret of the manufacture to Krafft, from whom it appears that Kunkel learnt what he knew, and published in the year 1678 a pamphlet on this remarkable product. In those early days phosphorus was a very costly body, being valued as one of the most remarkable and interesting of chemical substances. Krafft exhibited it as one of the wonders of nature to various crowned heads, among others, in the year 1667, to King Charles II. of England.

From the fact of the presence of phosphorus in bones, its universal diffusion in nature might have been suspected. In fact, upon a soil free from phosphorus no plant could grow, as its presence is essential to the formation of the seed, and is found in largest quantities in the seed and fruit. Phosphorus, likewise, is necessary for the growth and nutrition of the animal tissues, and is present both in the substance of the brain and in the nervous matter connected therewith. It ranks, therefore,

<sup>1</sup> Also  $Na_2O, K_2O, 0.30$ .

<sup>2</sup> A little fluorine included with the  $Fe_2O_3, Al_2O_3$ .

<sup>3</sup> The process consisted in distilling evaporated urine with sand in clay retorts.

like oxygen, nitrogen, hydrogen, carbon, &c., as one of the elements necessary to the building up of the animal and vegetable body. Besides being present in all fruitful soils, phosphorus is found in most springs, in all rivers, in the sea, and even, it is stated, in minute traces in the atmosphere (Barral). At one time phosphorus was considered to be a compound body containing 'phlogiston' and an acid, till Lavoisier investigated the subject in the year 1780, and showed that when phosphorus is burnt in air the acid produced weighed more than the phosphorus itself, the increase in weight being due to the oxygen of the atmosphere with which the phosphorus had combined (*Opuscules Physiques et Chimiques*, 1774).

Up to the year 1845 the 'yellow' or ordinary phosphorus was the only variety known. 'Red' or 'amorphous' phosphorus was discovered by Schrötter in 1845, although its existence had been previously observed by other chemists, who had misunderstood its nature. Other modifications of phosphorus will be referred to when discussing the general properties of the element.

Scheele's method of preparing phosphorus, first published in 1774 by Bouillon, in the year 1775, consisted in dissolving bone ash in nitric acid, and then removing the lime as sulphate with sulphuric acid; but this method was afterwards simplified by Nicholas and Pelletier, who decomposed the bone ash direct by sulphuric acid, improved by Fourcroy and Vauquelin, who determined the exact quantity of sulphuric acid required for the complete decomposition of bone ash.

#### THE MANUFACTURE OF PHOSPHORUS.

(a) *The Raw Materials.—Phosphates.* Of all the phosphates now to be had in the market pure bone ash is to be preferred, other things being equal, inasmuch as it contains a high percentage of calcium phosphate; it is easily decomposed by sulphuric acid; and it contains only small quantities of magnesia, oxide of iron, and silicious matter.

On the other hand, it has to be considered that bone ash probably costs more to-day, per unit, than any other form of calcium phosphate.

Pure bone ash (from ox-bone) possesses the following composition:—

	Per cent.
Phosphoric oxide . . . . .	39.55
Lime . . . . .	52.46
Magnesia . . . . .	1.02
Ferric oxide . . . . .	0.17
Carbon dioxide, alkalis, &c. . . . .	4.43
Water, carbonaceous matter, &c. . . . .	0.86
Silicious matter . . . . .	0.51
	99.00

Bone ash, as met with in commerce, varies considerably in composition, the amount of phosphoric acid existing as tri-calcium phosphate ranging between 27 and 37 p.c. It is obtained from the bones of South America, and is not obtained from m bones, but contains in addition the ash of other parts of the carcass. Subjoined is an analysis of commercial bone ash:—

#### Bone ash from South America.

	Per cent.
Phosphoric oxide . . . . .	33.68
Lime . . . . .	43.37
Magnesia . . . . .	1.14
Ferric oxide . . . . .	0.58
Carbon dioxide . . . . .	4.22
Alkalis . . . . .	0.62
Water, carbonaceous matter, &c. . . . .	6.70
Silicious matter . . . . .	9.69
	100.00

Another very suitable calcium phosphate, which is to be had in small quantities, is what is known as precipitated phosphate of lime. This substance is obtained as a by-product in the manufacture of glue from bones. The method adopted is a modification of the system proposed by Fleck (*Wagner's Chemical Technology*, p. 543). The bones, previously crushed and deprived by boiling of the fat they contain, are soaked in a weak solution of hydrochloric acid, until they become quite soft. The clear liquor, containing the calcium phosphate in solution, is drawn off from the cartilaginous substance, and milk of lime is cautiously added to it, in quantity sufficient to throw down the phosphates, which are then washed, dried, and collected. The following analysis of a quantity of this phosphate which was used in the manufacture of phosphorus will show what a very rich phosphate is obtained in this way:—

#### Precipitated Phosphate of Lime.

	Per cent.
Phosphoric oxide . . . . .	39.45
Lime . . . . .	44.88

This phosphate dissolves easily and gives an excellent phosphoric acid.

The next raw material to be referred to as a source of phosphorus is apatite. Apatite is a pure form of mineral calcium phosphate, combined with either calcium fluoride or calcium chloride forming the definite chemical compounds *fluor apatite*  $(3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)$  or *chlor apatite*  $(3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2)$ . The pure crystals of the former contain 42.26 p.c. phosphoric oxide, while the crystals of the latter contain 40.92 p.c. This last variety is not so largely imported. Fluor apatite comes from Canada, and also from Spain under the name of *Spangol*. The phosphates are of a light green color, and are found in the Ottawa district of Canada, in the volcanic rocks of New Jersey and New York, and other places in the American continent. They contain neither organic nodules nor fossils, as many other phosphates do, but have the phosphoric acid evenly distributed through large masses of the rock. The following analyses of two lots of Canadian phosphates will give some indication of their general composition:—

#### Canadian Calcium Phosphate.

	Per cent.	Per cent.
Phosphoric oxide . . . . .	33.51	37.68
Lime . . . . .	46.14	51.04
Ferric oxide, Alumina . . . . .		
Fluorine, &c. . . . .	7.83	6.88
Silicious matter . . . . .	11.90	4.29
Water and loss on ignition . . . . .	0.62	0.11
	100.00	100.00

The absence of carbonates makes the complete decomposition of this phosphate with sulphuric acid troublesome and tedious when large quantities.

A variety of apatite, called also *Estramadurite*, has the following percentage composition:—

*Spanish Phosphorite (Voelker).*

	Per cent.
Phosphoric oxide . . . . .	33.38
Lime . . . . .	47.16
Magnesia . . . . .	trace.
Carbon dioxide . . . . .	4.10
Sulphuric oxide . . . . .	0.57
Ferric oxide . . . . .	2.69
Alumina . . . . .	0.89
Fluorine . . . . .	4.01
Silicious matter . . . . .	3.71
Water . . . . .	3.59

100.00

is used in the manufacture of phosphoric acid, very suitable, both on account of its comparative freedom from iron and the presence of a certain amount of carbonates, is 'Sombrero phosphate,' obtained from the small uninhabited island of that name in the Caribbean Sea. It contains the following:—

*Sombrero Phosphate.*

	Per cent.
Phosphoric oxide . . . . .	35.12
Lime . . . . .	51.33
Ferric oxide and alumina . . . . .	1.02
Carbon dioxide . . . . .	7.40
Silica . . . . .	2.02
Alkaline salts . . . . .	0.42
Water and loss on ignition . . . . .	2.69

100.00

French phosphates contain from 50 to 75 p.c. of calcium phosphate. The high-class qualities should be found useful in this manufacture. The next phosphate to be referred to is 'Redonda phosphate,' both on account of its high percentage of phosphoric oxide, and also from the fact that this peculiar mineral has been the subject of many patents having for their object the utilisation of the phosphate. Redonda phosphate, which is a phosphate, comes from the West Indies; it contains no lime, the phosphoric oxide present being combined with iron and aluminium.

*Redonda Phosphates.*

	I.	II.
	(Readman)	
Phosphoric oxide . . . . .	35.47	39.71
Ferric oxide . . . . .	8.85	9.45
Alumina . . . . .	20.17	20.90
Silicious matter . . . . .	9.70	6.65
Organic matter, and water of combination . . . . .	7.20	22.86
Moisture . . . . .	18.61	
	100.00	99.57

The processes proposed for working this phosphate will be referred to subsequently. The last mineral phosphate to be mentioned in connection with this part of the subject is what is known in the market as Charleston

phosphate. This is not a high-class phosphate, like some of those considered, nor is it very free from iron and aluminium, but it has the property of being easily and uniformly decomposed when treated with sulphuric acid, and is of very regular composition. Charleston phosphate is found in the beds of several of the rivers and on the lands of South Carolina. The river phosphate differs slightly from that of the land both in colour and hardness; moreover, in the river phosphate the iron exists partly as pyrites, while in the land phosphate it exists as ferric oxide. The river variety is that usually sent to this country, being richer in phosphates. It is obtained by dredging the river, and is dried by hot air before exportation.

*Charleston Phosphate (Readman).*

	Per cent.
Phosphoric oxide . . . . .	27.17
Sulphuric oxide . . . . .	3.30
Carbon dioxide . . . . .	4.96
Lime . . . . .	44.03
Magnesia . . . . .	0.37
Alumina . . . . .	1.44
Ferric oxide . . . . .	0.43
Ferric sulphide . . . . .	3.60
Alkaline salts . . . . .	0.87
Fluorine, &c. . . . .	2.38
Combined water and loss on ignition . . . . .	4.60
Sand . . . . .	5.60
Moisture . . . . .	1.25

100.00

This enumeration does not by any means exhaust the various phosphates available for the production of phosphorus; but the list here given of crude materials which are, or which may be, employed in the manufacture, will convey an idea of the resources at the disposal of phosphorus makers.

It may be added that whichever variety of phosphatic material be employed, it is absolutely essential to reduce it to a very fine state of division as a preliminary step in the manufacture.

It should be remembered that the presence of iron, alumina, magnesia, and alkalis—as also any excessive amount of carbonates—is objectionable. The former substances are dissolved, to a great extent, during the sulphuric acid treatment, and reappear at a later stage, in the phosphorus retorts, while carbonates, of course, consume their equivalent quantity of sulphuric acid, and thus add to the cost of production.

As has been indicated, however, a certain limited quantity of calcium carbonate is advantageous in the sulphuric acid treatment, as it materially assists the decomposition of the phosphatic material operated upon.

The amount of calcium carbonate should not exceed, say, 10 to 12 p.c. for economical work.

Generally speaking, a high-class phosphate should be selected—one containing at least 70 p.c. of calcium phosphate. These are now easily obtained in large quantities, the advantages of employing them are very great.

With respect to the other material used in the manufacture of phosphorus (at least in the

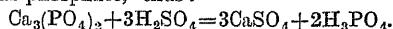
initial stage.)—namely, sulphuric acid—it will suffice to say that ordinary chamber vitriol of sp.gr. 1.500 to 1.600, free from arsenic, is quite suitable for decomposing the calcium phosphate into calcium sulphate and phosphoric acid.

(b) *The preparation of phosphoric acid.* In this, as in subsequent processes, the author will describe the plant (alluding incidentally to noteworthy matters) which, from personal practical experience, he has found to yield good results.

The decomposition of calcium phosphate by sulphuric acid is performed in a circular wooden vessel, shaped like a brewer's mash tun, 10 ft. in diameter and 8 ft. deep, provided with an upright wooden agitating shaft carrying three arms placed at regular intervals between the bottom and middle of the vessel.

The only ironwork in the interior of the decomposing vessel consists of a cast-iron shod on the lower extremity of the revolving shaft, and a strong cast footstep in which it works. The revolving arms are simply tenoned into the upright shaft. Pitch pine 3 ins. thick is preferably employed in the construction of the decomposer, and before use the tun is thoroughly impregnated with tar-oil, which acts as a preservative to the vessel in good repair for many years. It is securely bound by strong hoop iron, which may with advantage be protected by sheet lead at any part exposed to the drip of acid. The agitator is driven by a crown wheel and pinion, connected in the usual way with a steam engine. At the lower circumference of the tun, as near the bottom as possible, a wooden man-hole door is provided, and this, opening outwards, allows the charge to be run out to the adjoining filters.

The operation of decomposing the calcium phosphate is thus conducted. The tun is filled to the depth of about 18 ins. with weak liquors from a previous decomposition, and to this is added about 2 cwt. of calcium phosphate. High pressure steam is then blown in by a lead pipe, until the liquor boils, when the steam is shut off. The agitator is now put in motion, and charging is commenced, adding alternately, say, 6 cwt. of finely-ground phosphate, and 5 carboys of chamber sulphuric acid (sp.gr. 1.500 to 1.600), till the whole has been introduced. A convenient charge for such a decomposer as has been described is from 80 cwt. to 100 cwt. of phosphate, and the equivalent quantity of sulphuric acid necessary to decompose into sulphate the *total lime present*, existing either as carbonate or as phosphate,<sup>1</sup> thus :



It is advisable not to introduce the charge too rapidly, but rather to allow ample time for a uniform decomposition to take place. The charging should be completed in three hours, and it is well to continue the agitation an hour, or even more, until all visible action has ceased.

When it is ascertained that the decomposition is complete, the large man-hole door is gradually opened, and the entire contents of the

tun run off by a shoot to one of a series of filters, conveniently arranged below the level of the decomposer, agitation being still maintained.

The filters are rectangular wooden tanks, each about 20 ft. long, 16 ft. wide, and 2½ ft. deep. They are not set level, but are laterally inclined at a gradient of about 1 in 30, so as to drain towards ten exit holes pierced along the lower side. The filtering medium consists of ashes. Coarse 'clinkers' are spread evenly over the floor and a layer of sieved ashes above, the entire depth of the filtering bed being about 6 ins.

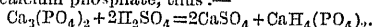
The filtering tanks are securely bound with tie rods, and before use the woodwork is impregnated with light tar-oil. As it drains from the filters, the phosphoric acid liquor is caught in a wooden launder, common to the series of outlets on the filter tanks, and is conveyed by it to wooden lead-lined tanks in which strong liquors and weak washings are kept apart.

The strength of the solution at first draining from the filters is about 30°Twad. (sp.gr. 1.150). The flow must not be allowed to proceed too rapidly, as if the bed of gypsum or 'sludge' in the filters is allowed to dry it will crack on the surface, and a very imperfect washing will be the result. A spray of water is run over the gypsum by a perforated pipe running along the higher side of the filter tanks. This spray is so regulated as to keep the sludge covered with 1 or 2 ins. of water until the end of the operation. The upper surface of the gypsum is carefully raked every few hours with a wooden mud-rake, so as to fill up any cracks through which the washing water might find too ready an exit. The spray is continued until the effluent washings are 2°Twad. (sp.gr. 1.010). The water is then turned off, and the sludge is allowed to dry, being finally piled up to permit the last trace of washings to drain from it. The gypsum is then removed from the filter tank to undergo artificial desiccation.

The phosphoric acid draining from the filters is considered 'strong liquor' until it falls below 10°Twad. (sp.gr. 1.050), and this first fraction is reserved for concentration. The latter fraction, between 10°Twad. and 2°Twad. (sp.gr. 1.050 and 1.010), is employed partly for the decomposition of a further lot of phosphate, as has been described, and partly for the first washing upon the filter before the water spray is turned on. Both fractions are blown by means of Körting's or other elevator, such as an 'acid egg,' to stock tanks, from which the evaporating vessels, and the decomposer or filters, can be supplied by gravitation.

The *gypsum sludge*. The wet sludge removed from the filters contains water, phosphoric acid, and undecomposed calcium phosphate in quantities varying according to the care bestowed on the operations described. The sludge may be dried upon a bed formed of fireclay-covers over flues heated by any available waste heat. When sufficiently dry, the gypsum is passed through a sieve to break up the larger lumps, and is in this state sold to manure makers as a dryer for superphosphates; or it is used to fix the ammonia in the 'compost heaps of the farmer, and for other purposes.

<sup>1</sup> This statement differs from that given in most of the text books on Chemistry, which state that sulphuric acid is added in quantity only sufficient to form the acid calcium phosphate, thus:—



(d) *Concentration of phosphoric acid liquor from the filters.* This may be accomplished either in shallow rectangular wooden tanks, lined with 10 lbs. lead, and provided with lead pipes (1½ in. diameter, and 20 lbs. lead to 1 ft.) through which high-pressure steam is allowed to pass; or it may be performed in a cast-iron saucer-shaped pan, also lined with lead and having steam coils as before. During evaporation the liquor is maintained in motion by an agitator, provided with arms, and driven as usual by power. The latter system is the one to be preferred. Agitation of the liquor during concentration, however, during the evaporation, prevents the deposition of gypsum on the steam coils, a result which is very common in any unstirred evaporator. Such acid liquor, if allowed to form, becomes extremely hard and difficult to remove without injury to the lead pipes.

The stronger phosphoric acid from the filters

—that above 10°Twad.—is allowed to flow by gravitation from the stock tank to the evaporator, to be concentrated till the clear yellow-coloured phosphoric acid attains a strength of from 65°Twad. to 100°Twad. (sp.gr. 1.325 to 1.500), according—as will be immediately explained—to the selected method of treatment. During the evaporation nearly all the calcium sulphate held in solution is precipitated, so that the concentrated acid liquor retains only a very small quantity of lime. Almost all of this lime ultimately deposits as sulphate after settling in the stock tank. As the phosphoric acid liquor becomes more and more concentrated, some of the free sulphuric acid which may be present is expelled during the evaporation—the steam or vapour from the evaporator having frequently a strong acid reaction. The following are some analyses of phosphoric acid liquors at various strengths made from phosphates which are not named:—

	Strength				
	58°T.	69°T.	72°T.	86°T.	90°T.
Uncombined phosphoric acid ( $P_2O_5$ ) . . . . .	19.30	27.60	29.20	34.02	36.44
Combined phosphoric acid ( $P_2O_5$ ) . . . . .	4.68	3.61	3.60	4.40	4.80
Sulphuric acid ( $SO_3$ ) . . . . .	2.47	1.40	0.70	—	1.39
Alumina and ferric oxide, &c. . . . .	1.92	2.56	—	3.26	3.61
Lime . . . . .	—	1.00	—	0.84	[trace
Water . . . . .	71.63	63.83	66.50	57.48	53.76
	100.00	100.00	100.00	100.00	100.00

The gypsum deposited in the evaporators or in the stock tank may either be washed by itself on a small filter, or it may be removed to the large acid filter, and be washed along with the acid liquor. If conveniently done, the latter method is more economical.

The concentrated acid is cooled in lead-lined store tanks, where, as has been said, the last traces of calcium sulphate are deposited, and the acid is then ready for the next operation of mixing with carbon and drying.

(e) *Mixture for the retorts.* The concentrated phosphoric acid may now be mixed with coarsely-ground wood charcoal, coke, or sawdust, and carefully dried in a cast-iron pot or muffle furnace. Sawdust absorbs a large quantity of liquor, so that when it is employed concentration of the acid liquor to the minimum sp.gr. of 1.320 is inadmissible, and, when thus saturated, it can be removed without loss through sweating.

On the other hand, its greater bulk and low specific gravity present objectionable features. If sawdust be employed, the mixing may be accomplished on a clean brick or asphalt floor and the mixture may be carefully charred in a

If coke or charcoal be used, the preliminary concentration of the phosphoric acid to a syrupy consistence is indispensable, and the mixing should be done in a cast-iron pot, in which the charge is subsequently dried by fire-heat from beneath. The amount of fixed carbon required is about 25 p.c. by weight of the concentrated

acid liquor. Great care must be taken with the drying of the charge. The heat must be regular and not too high, and when it is completed the charred mass must be carefully preserved from air in malleable or cast-iron boxes provided with closely-fitting lids, and conveniently situated for the retorts.

(f) *The description of the clay retorts, their manufacture, and details of the clay employed.* The retorts in which the charred mixture is distilled are made of Stourbridge freclay. The retorts are shaped much like a bottle. The accompanying section shows the appearance they present.

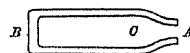


FIG. 1.—PHOSPHORUS RETORT MADE OF STOURBRIDGE CLAY.

The total length A to B is 3 ft. The internal diameter is about 8 ins. The clay is about 1 in. thick, except at B, where it is about 1½ ins. The neck is tapered from C to A, where the thickness is 3 ins. Into this narrow orifice a 2-inch mal. iron pipe leading to the condenser is luted, and can be easily removed to empty and charge the retorts.

The retorts should be made at the phosphorus works; the clay employed is such as is used for glass-house pots, and is tolerably free from iron, rich in silica, and comparatively low in alumina. The clay, as generally supplied from Stourbridge, has previously undergone the operation of 'weathering' for many months.

This renders it plastic, more easily worked, and much more durable when made into retorts.

A mixture which has been successfully employed for the construction of retorts consists of two parts of the raw clay, finely ground, carefully mixed with one part of the calcined clay coarsely ground.

The mixture is allowed to 'sour' or season for three or four weeks by incorporating it with water to a thick doughy consistence, and leaving it piled up in a low flat heap, about 16 ft. long and 3 ft. in depth, after which it is ready for moulding into retorts. The apparatus required for the latter is not very elaborate. It consists of a turntable or wheel, upon which the retorts are built, and a sheet-iron mould about 3 ft. long, divided into two lengths of about 18 ins. each, with a fishing-rod joint to connect the one to the other.

On the turntable a loose base-piece of plank, about 12 ins. square, is first placed, to support the mould containing the soft clay retort during its removal to the drying room. Wooden beaters, and a flat circular disc, 6 ins. in diameter, with a shaft, like an old-fashioned churn stirrer, are also required.

Before commencing to build a retort, the inside of the iron mould is smeared over with oil to prevent the clay adhering to the iron. This done, the lower half of the sheet-iron mould (which is about 1 foot in diameter) is placed on the square board surmounting the turntable (a small quantity of sand having been first sprinkled over the board). The clay in a tough plastic state is introduced into the mould. This is worked by the hand to the shape of the bottom part of the retort. The clay is well beaten to the side with the wooden beater, and the bottom is pressed hard down by a circular disc. When the lower half of the retort is constructed in the way described, the upper portion of the iron mould is then jointed on, and this is likewise built up with clay in the same way until the whole retort is completed.

Some skill is required in making the tapered neck, but experienced workmen have little difficulty in doing this. The retort with the mould is now ready for removal to the stove-room, which should adjoin the retort house. The temperature in the heated room is maintained at 90°F. by means of flues below the floor. After remaining about a week in this room the retorts have shrunk sufficiently to admit of the moulds being withdrawn. When this is done, the outer skin of the retorts which was next the moulds has its hollows carefully filled up with damp clay. The retorts are then washed with a thin emulsion of clay and water until the outer surface is smooth and free from cracks or holes. They remain in this room for at least 3 weeks longer, or until they are required for use. Retorts with cracks or flaws are here rejected.

When starting a new bench of retorts, or when restarting a furnace that has been off for repairs, the retorts may be taken direct from the stovehouse and placed in the cold furnace. The fire is lighted, and the heat gradually raised to the temperature necessary for the manufacture of phosphorus.

In actual work, however, it is a common experience to find two or three retorts in a fur-

nace broken, and, in order to replace these without interruption of the usual work, it is necessary to take the required number of new retorts from the stove-house, and place them in a special kiln, to be slowly heated to the temperature of the working furnace which contains the

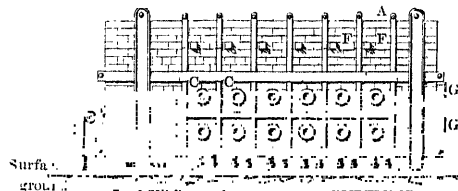


FIG. 2.—PHOSPHORUS FURNACE.  
(Side elevation.)

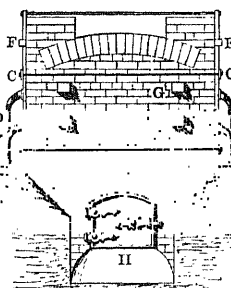


FIG. 3.—PHOSPHORUS FURNACE.  
(Front elevation.)

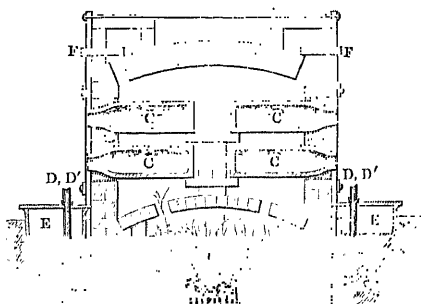


FIG. 4.—PHOSPHORUS FURNACE.  
(Transverse section through A-B, Fig. 2.)

C. Phosphorus retorts. D, D'. Pipes to condenser.  
E. Condensing trough. F. Dampers. G. Spyholes.  
H. Fire door.

broken retorts. When this temperature has been attained, the new retorts are quickly removed from the kiln and are placed in the working-furnace, the broken ones having of course been first removed.

(g) *The Phosphorus Furnace.* The furnace used in the distillation of phosphorus is of the

galley type, similar to that employed in the distillation of zinc by the Belgian process. A convenient size holds twenty-four retorts, twelve on each side, arranged in two tiers—that is, six retorts on each tier. The retorts are placed back to back, their necks protruding slightly (1 in.) through the side walls of the furnace. The closed ends of the retorts are supported by a 9-inch wall, having fireclay covers built into it over the spaces into which the ends of the lower tier are inserted. This wall divides the furnace longitudinally. The furnace measures about 12 to 13 ft. long and about 7 ft. broad, outside dimensions. The firegrate is  $5\frac{1}{2}$  ft. in length by  $1\frac{1}{2}$  ft. in breadth, and the firebricks are made of 2-inch square wrought-iron. Over the firegrate, about  $2\frac{1}{2}$  ft. above the bars, a  $4\frac{1}{2}$ -inch firebrick arch is thrown. This arch has six ports on each side, corresponding to the six retorts, and these are so placed that the fire ascends between each pair of retorts. The arch extends from end to end of the furnace. Upon the top of this arch the 9-inch wall previously mentioned is built. This wall is about 2 feet in height, and is sufficiently high to allow the ends of the upper tier of retorts to rest on the top of it, the ends of the lower tier resting on covers built into the wall about 6 ins. above the arch which covers the fire. The outer walls of the furnace are 9 ins. thick, and the outer arch which incloses the whole is also made of 9-inch firebrick. The retorts are, in fact, simply suspended in what is practically two flues in one furnace, the walls of which are the outer walls of the furnace and the 9-inch central dividing wall.

The furnace must be very firmly bound, both longitudinally and transversely. This is all the more required as the walls of the furnace must necessarily be thin, and, moreover, each retort has a 12-inch square port-hole through which it is primarily introduced into the furnace. All these circumstances, tending to weaken the side walls, point to the necessity of securely and substantially binding the furnace.

(Figs. 2, 3, and 4) will show the construction and arrangement of the furnaces and side condensing troughs.

The heat from the fire ascends through the ports of the  $4\frac{1}{2}$ -inch arch described above, and passes through the chambers in which the 24 retorts are hung, and then it escapes through 6 ports of the upper 9-inch arch to small flues built on either side of the top of the furnace. The products of combustion now travel along these flues and descend at the back of the furnace furthest from the fire to the main flue. If required, this waste heat may be first utilised to dry the gypsum from the phosphoric acid filters. The firebricks used in the construction of the furnace must be of the very best description, and none but a most experienced furnace-builder should be intrusted with the erection of it. Dampers are placed on each of the upper port-holes, and a large damper where the two small flues unite with the main flue. Spyholes should be placed on the front wall of the furnace, so that the chambers containing the retorts can be conveniently viewed. This is a most important provision, and should in no case be neglected, as frequently retorts are cracked, and there is no

other means so simple as the spyhole to ascertain their condition. When starting a new furnace great care must be taken not to raise the heat so rapidly as to cause cracks in the walls, which would admit cold air and be fatal to the retorts; and, when the necessary heat has been attained, as much caution is required to maintain a steady temperature. Clay retorts are very sensitive to sudden changes of temperature, and the life of a retort largely depends upon its treatment in this respect.

(h) *The Distillation.* The 24 retorts having been placed in the port-holes in the manner described, their necks are built in with broken bricks and fireclay to prevent access of air into the interior of the furnace. The fire is now lighted and the heat very gradually increased, care being taken during this time to have the dampers only slightly open. After 18–24 hours firing the retorts should be at a bright-red heat and ready for charging. This is done by means of a scoop, made out of a 3-inch iron pipe, which has been opened up and provided with a handle. The scoop is about 18 ins. long, and made so as to enter the 3-inch neck of the retort without difficulty.

The retorts hold conveniently about 20–30 lbs. of the charred mixture. It is advisable not to fill them more than two-thirds full. This does not take more than a few minutes to accomplish, and whenever it is done the 2-inch malleable iron pipe leading to the condenser should be at once luted on. Various forms of condensers may be employed. A suitable arrangement consists in having long troughs on each side of and close to the furnace (as shown in Figs. 2, 3, and 4) made of light cast-iron, about 12 ft. in length by 18 ins. broad by 24 ins. deep at one end and 18 ins. at the other end. The lip of these tanks has a 3-inch flange on the outside, upon which the cast-iron cover is bolted. Twelve 3-inch cast-iron pipes with faucets pass through this cover, and dip an inch or two into the water with which the trough is partially filled. These short pipes are so placed that the 2-inch malleable iron pipes before referred to can be conveniently luted to their faucets, and thus connect the retorts with the condenser.

The water in these troughs soon becomes warm with the hot gases bubbling through it. This is advantageous, as it prevents solid phosphorus choking up the pipes. The bottom of the troughs being deeper at the one end than at the other causes the melted phosphorus to run down to the lower end, from which it can be removed from time to time by ladles.

The incondensable gases are removed from the trough by a 10-inch pipe, and can either be sent at once to the stalk or connected with further condensing arrangements. Care must be taken when charging the retorts to avoid spilling any of the charge into the condensing troughs, and to insure this it is well during the operation to employ sheet-iron trays which cover the open faucets.

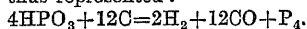
The luting used for the 2-inch pipes, both at the retort and faucet ends, is a mixture of clay, with salt, or with a small amount of oil, added to prevent cracking. After the retorts are all charged, the heat is raised to a temperature



approaching whiteness. The odour of sulphurous acid may then be detected in the escaping gases, especially if the charged mixture has not been sufficiently dried. Sulphides are next discoverable, and lastly, in about two or three hours, phosphorus. The distillation should be completed in about 16 hours, and after withdrawing the residues from the retorts and slightly cooling the furnace, the charging can be recommenced as before. Retorts, if carefully attended to, may last a considerable number of distillations.

When the temperature is fully up and phosphorus is coming off vigorously, the retorts should be examined by the spyholes, when the smallest flaw can be easily detected by the bright dazzling phosphorus flame which issues from the smallest crevice. When this is observable the retort should have its charge withdrawn, and the retort itself is then taken out and replaced by one from the kiln heated to the temperature of the phosphorus furnace, as has been already described. There is no difficulty in doing this, as the ports are intended to permit this very operation.

The chemistry of the process of preparing phosphorus from *osmundum* may be described as follows: Phosphoric acid liquor ( $H_3PO_4$ ), after being mixed with carbon and heated to a dull red heat, is resolved into metaphosphoric acid ( $HPO_3$ ), and when this is further heated to a high temperature in the retorts it is broken up by the carbon originally added and phosphorus distils over. The change may be thus represented:



An example of the yield, &c., from a known amount of phosphoric acid may be of interest.

(Quantities taken:—

502 lbs. of phosphoric acid liquor containing 25.7 p.c. free  $P_2O_5$ .

137 lbs. of coarse wood charcoal.

These were mixed together and dried in the manner described.

The dried mixture weighed 380 lbs.

On distillation the following results were obtained:—

Residue in retorts weighed 67 lbs.

Yield of refined yellow phosphorus, 38 lbs.

Theoretical yield, 56.2 lbs.<sup>1</sup> (Yield = 67.5 p.c.)

(i) *The Crude Phosphorus.* The phosphorus obtained in the condensers varies very much in appearance from a pale buff to a brick-red chocolate, or nearly black, colour. The colour is no doubt due to impurities, as well as to the presence of lower oxides of phosphorus and amorphous phosphorus. If condensed in cold water, it resembles the raspings of cork and floats on water. The crude product is ladled out of the condensing trough into malleable iron boxes provided with handles, in which it is carried to the refinery. Phosphorus in this condition is much more inflammable than it is in a pure state, and great care must be observed in the handling of it.

(j) *The Refining.* There is always more or less sand and clay mingled with the crude phosphorus, partly due to the unavoidable dust in the furnace-house and also to the luting. To

get rid of this, it is advisable to fuse the crude product under hot water, and, after a thorough stirring with a wooden rake, to allow the mass to solidify, when it can be easily broken up with chisels, and is then of a uniform character.

The sand, clay, &c., mixed very frequently with some phosphorus, are left on the upper surface in a loose pulverulent condition. If these impurities are found to contain phosphorus, they may be distilled in an iron retort and the phosphorus recovered.

The solidified phosphorus is now ready for refining. The method described in text-books is to squeeze the melted phosphorus through chamois leather. A more rapid method is either to distil it in an iron retort or to refine by the use of chromic acid. The last method is probably the one most to be recommended. To carry out the refining by this process the crude phosphorus is first fused under water in a small lead-lined agitating pan provided with a lead steam-coil, and from 3-4 p.c. of potassium or sodium dichromate (previously dissolved in water) is added. Sulphuric acid is then added, and the solution is next run into the

left to mix for 2 hours. The phosphorus should be of a pale-yellow colour and almost transparent. The chrome liquors are now carefully syphoned off, and the phosphorus then receives a washing with hot water, after which it is rapidly filtered through a mechanical filter to remove the mechanical impurities. The phosphorus is now ready for moulding.

(k) *The Moulding.* The phosphorus melted under hot water may now be cast into 'wedges,' or made into 'sticks.' The 'wedges' or 'pains' (of the French manufacturer) are easily made. The liquid phosphorus is ladled under hot water into tin moulds 10½ ins. diameter by 4½ ins. deep, standing in a row in a shallow trough, and while still liquid a star-shaped arrangement, made also of tin, is dropped into the mould. The object of this is to divide the circle equally into 10 sectors or wedges. On solidifying the phosphorus by running in cold water into the trough and then removing it from the mould,

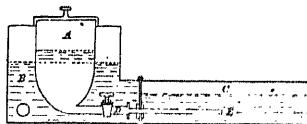


FIG. 5.—SECTION OF APPARATUS FOR MOULDING PHOSPHORUS INTO STICKS.

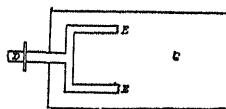


FIG. 6.—PLAN OF COLD WATER TANK FOR MOULDING PHOSPHORUS INTO STICKS.

A. Pot for melting phosphorus under water. B. Hot water tank heated with steam coil. C. Cold water tank, flanged to B. D. Cook for escape of liquid phosphorus. E. Metal tubes. (Same letters apply to Figs. 5 and 6.)

10 separate wedges are obtained in a convenient form for packing, each wedge weighing about

<sup>1</sup> From phosphorus in free  $P_2O_5$ .

2 lbs. To admit of easy removal of the phosphorus, the tin mould divides into 2 parts and is made tight by india-rubber &c.

If the phosphorus is of 'sticks,' the fused element is drawn through glass tubes in an apparatus illustrated by the sketches (Figs. 5 and 6).

Another method of moulding is to run the liquid phosphorus into tin tubes made of a length to suit ing-cases. The tubes are closed at one end by corks, and are set (corked end down) in troughs containing hot water, when the tubes are filled with the molten phosphorus. Cold water is run into the trough to solidify the latter, which is then removed from the moulds.

(1) *The packing.* The 'wedges' are packed along with water in tin cylinders, holding 50 kilos. of phosphorus. The dimensions of the cylinders are 22 ins. deep by 11 ins. diameter. The lids (11 ins. diameter) are loose, but fit tightly inside, and have a  $\frac{3}{4}$ -inch hole, through which water is poured after the lids are soldered on. These small holes are finally soldered up, and the cylinder is thus hermetically sealed and completely filled with water. Another size of case sometimes employed holds 25 kilos.; it is 12 ins. deep by 11 ins. diameter.

The tin packing cylinders should be provided with three wire handles—two opposite one another—at the upper part, and the third lower down near the base. These are found convenient in handling.

The sealed tins are now packed along with sawdust in rectangular wooden boxes 24 ins. long by 12½ ins. broad × 12½ ins. deep. The wood is pine  $\frac{3}{4}$  in. thick. The boxes should be strengthened with hoop-iron at the edges. The sawdust is tightly rammed down between the tin case and the side of the box, and thus makes a firm and safe package.

When exporting phosphorus to certain countries—e.g. Germany—the wooden boxes require to be further packed in canvas, and iron handles must be tightly fixed to either end of the box for convenience in lifting.

The 'stick' phosphorus is packed along with water in tins which hold 10 lbs. each. The tins are 7½ ins. long by 5½ ins. diameter; each one holds about 90 sticks (7½ ins. long by  $\frac{1}{2}$  in. diameter).

The lids, &c., are soldered on as before described. These tins are further packed as in the case of 'wedges,' in wooden boxes holding ten in a box.

(a) *Other proposed methods of manufacture.* Phosphorus is mixed with lead phosphate with nitric acid and acetate) with finely distilled for phosphorus.

(2) Fleck proposed to combine the manufacture of phosphorus with that of glue and gelatin. By this method the bones, freed from fat, are treated with weak hydrochloric acid, leaving the cartilaginous matter insoluble. The acid phosphate liquor is evaporated, mixed with carbon, and distilled in suitable retorts.

(3) E. C. Mantrand (Eng. Pat. 1166, May 25, 1854) patented a method of preparing phosphorus by decomposing an intimate mixture of

calcium phosphate, carbonaceous matter, and silicious matter at a bright red or white heat in an atmosphere of hydrochloric acid or chlorine gas, when phosphorus, phosphoretted hydrogen, carbon dioxide, &c., distil over.

(4) Wöhler suggested the method of decomposing calcium phosphate with silica and carbon, and distilling.

(5) Gentele, in 1857, published a plan of phosphorus manufacture combined with the preparation of sal ammoniac. He treats the bones with hydrochloric acid. To the resulting solution crude ammonium carbonate is added. The precipitated calcium phosphate so obtained is employed in the preparation of phosphorus, while the solution of ammonium chloride is evaporated and sublimed for sal ammoniac.

(6) Gerland (in 1864) suggests the treatment of bones with an aqueous solution of sulphurous acid.

(7) Minary and Sourdray (1865), proposed to treat bones with a mixture of iron and coke.

Various patents have been taken for the following methods of preparing phosphorus:

E. Lammy (Eng. Pat. 311, 1857) grinds ammonium phosphate with carbon, dries, and distills, producing first ammonia and then phosphorus.

E. A. Brooman (Eng. Pat. 2294, 1864). Silica, iron, and coal are added to calcium phosphate in such proportion that silica can form with lime a fusible slag, and iron phosphide is obtained. This latter may then be heated to quick redness with sulphur, sulphuretted hydrogen, carbon disulphide, &c., &c., to obtain phosphorus.

J. H. Player (Eng. Pat. 660, 1866, and 1064, 1867) mixes phosphoric acid liquor evaporated to a thick paste with (1) spent tan or (2) with coal or coke in fine powder. He then carbonises to remove volatile matters, and distills the residue in clay retorts in the usual way.

E. Aubertin and L. Boblique (Eng. Pat. 2458, 1867) (1) mixes fine ground calcium phosphate with twice its weight of silica and 25 p.c. of coke, and heats to orange-red or white heat, when phosphorus comes off *without fusion*. No apparatus is described.

Claude Brison (Eng. Pat. 3515, 1868) patents the employment of a blast-furnace and blowing engine in the manufacture of phosphorus, and also the admixture in the blast-furnace of the fuel with the materials for producing the phosphorus. 'The mixture employed by preference for producing the phosphorus consists of calcium phosphate, silica, and carbonate of soda; the whole thoroughly desiccated.'

E. Aubertin (Eng. Pat. 1593, 1870) secured a further patent for producing phosphorus from calcium phosphate, silica, and carbon. *1st process:* by fusion in a furnace or retort at a temperature of 2192° to 2404°F. *2nd process:* by fusion. Apparatus in this case is by preference a 'Fluss-oven' blast-furnace, and the temperature is 2192°–2932°F.

J. H. Player (Eng. Pat. 3501, 1872) proposes to utilise the waste gases from the retorts by passing them through a solution of copper sulphate, whereby copper phosphide is obtained.

Wagner's Chemical Technology, p. 544.

J. Townsend (Eng. Pat. 1862, 1872) distills Redonda phosphate either along with carbon and a flux of common salt or borax, or with a mixture of potassium and sodium sulphates, and so obtains phosphorus.

J. P. Serve (Eng. Pat. 49, 1879) employs a furnace—either a reverberating or blast-furnace—or retorts, and claims (1) 'the preparation, in the form of blocks or bricks, of intimate mixtures and in suitable proportions, of phosphates of lime, &c., &c., and of silica or other silicious body bound or held together by a carburetted body such as tar-pitch or coal.' (2) The extraction of the phosphorus from the blocks or bricks. (3) a special construction of blast-furnace and condensers.

A. Nicolle (Eng. Pat. 1693, 1888) decomposes min- with nitric acid, and treats the with potassium sulphate. He then filters from the calcium sulphate which is precipitated, and treats the filtrate with mercurous nitrate, thus obtaining mercury phosphate. This is washed, dried, and distilled with carbon, when mercury is first obtained, and then phosphorus.

J. B. Readman (Eng. Pat. 14962, 1888) claims the application of heat produced by passing an electric current through the materials containing phosphorus placed in a closed furnace.

Parker and Robinson (Eng. Pat. 17719, 1888) claim the employment of electricity on similar line- patent.

(Eng. Pat. 13240, 1890) for a process for the simultaneous manufacture of phosphorus and of alkaline silicate—(1) by heating a mixture of the phosphate with one or more alkaline sulphates or carbonates with or without the addition of silicic acid or a flux in a reverberatory furnace, or in retorts within a regenerative gas-furnace, lixiviating the resulting mass, and solution to obtain the alkaline ; 2, heating a mixture of the alkaline phosphate so obtained with silica and carbon in retorts placed in a regenerative furnace, thereby effecting the simultaneous production of phosphorus and an alkaline silicate.

Coignet (Eng. Pat. 2970, 1891) claims improvements in the moulding of phosphorus to avoid the carriage of much water in the packing cases.

The author has conducted a large series of experiments (*v. J. Soc. Chem. Ind.*, vols. 9, 10), with the view of obtaining phosphorus by distillation *direct* from the raw phosphate of lime, without the employment of sulphuric acid at all or the preparation—as an intermediate stage—of phosphoric acid. He has proved conclusively that silica in the form of sand, ganister, or flints intimately mixed with calcium phosphate and carbon, in suitable proportions, is capable, at a high temperature, of effecting the decomposition of the phosphate, expelling practically all the phosphorus contained in the mixture, leaving, as a residue, a fluid slag. Further, that with adequate condensing appliances a very large proportion of the phosphorus can be collected. Other phosphates, such as phosph- &c., provided fluxes suitable for each case are employed.

Retorts were found unsuitable for the distillation, both on the score of economy and durability, and the blast furnace, which was tried for some time, presented many practical difficulties in its working.

The success of the application of electricity to the production of certain metals and alloys, notably those of aluminium, led him to try that source of energy for the production of phosphorus, and the result has been that the author, along with T. Parker (who applied for letters patent only a few weeks after the author's application) (Readman's patent, 14962, Oct. 18th, 1888; Parker and Robinson's patent 17719, Dec. 5th, 1888) arranged for the erection of a large engines, dynamos, and turning out about 40 cwt. of phosphorus per week.

The object which has now been successfully attained in the new process, called the Readman-Parker and Robinson system, is the *continuous* production of phosphorus *direct* from raw materials by means of the electric furnace, the heat being applied in and through the phosphorus-bearing mixture in the furnace, and not, as in the case of distillation, in retorts, heated from the outside, involving, in consequence, a great expenditure of fuel.

The process is carried out as follows. The phosphate, carbon, and fluxes, in proper proportions and all carefully and intimately mixed together, are introduced (previously heated to as high a temperature as possible) into the upper part of the electric furnace by means of a tight-fitting hopper arrangement, the electric current is led to and from the furnace by copper cables connected to large carbon electrodes situated on either side of the furnace. The furnace itself is practically an iron tank, lined inside with refractory bricks, thus making a kind of brick-sided trough about 18 inches square and 36 inches deep, closed at the top by the hopper referred to, and having an outlet pipe to the condenser placed on the upper part of the side of the furnace.

After the charging of the furnace, the current is turned on, and soon indications of phosphorus may be seen in the condensers. The gases escaping by the side pipe pass on to a series of copper condensers, the first of which contains hot and the others cold water, when they are allowed to escape into the air. As the phosphorus is distilled off from the mixture the residue in the furnace forms a liquid slag, which from time to time is removed from the bottom of the furnace, fresh mixture being introduced by the hopper at the top precisely as in blast-furnace practice, where closed tops are used. In this way the operation is made continuous, and is carried on for days without cessation.

The mixed materials, as introduced into the electric furnace, can be had to contain about 14 p.c. of elementary phosphorus, and as the weight of the slags from these is not so much as half the weight of the original mixture, and as, moreover, the slag on an average contains only about 1 p.c. of phosphorus, it will be apparent that the decomposition is remarkably complete.

The crude phosphorus obtained in the condensers is refined in the way previously described.

The advantages of this process may be summarised as follows. No sulphuric acid is required, no need to prepare and concentrate phosphoric acid, much less handling of materials, no fire-clay retorts employed, long term stable process, larger yields, and less waste of coal.

#### THE PRODUCTION OF AMORPHOUS PHOSPHORUS.

Amorphous phosphorus in compact pieces is a reddish-brown, moderately hard substance,<sup>1</sup> somewhat resembling in appearance the hematite iron ore of Cumberland. It is opaque, with a slight metallic lustre. It is brittle and easily broken, and exhibits a conchoidal iron-black fracture with sharp edges.

The sp.gr. of amorphous phosphorus is 2.25. It is without taste or smell, is unattacked by most solvents, and if taken internally is excreted unchanged.

Amorphous phosphorus, as met with in commerce, frequently contains small quantities of ordinary phosphorus, from about  $\frac{1}{2}$  p.c. downwards according to Fresenius; in addition, it usually contains phosphoric acid, graphite, and other impurities, and has generally an acid reaction.

The following is an analysis of amorphous phosphorus:—

	Per cent. (Readman)
Phosphorus . . . . .	93.44
Phosphoric acid . . . . .	3.58
Ferric oxide and alumina . . . . .	0.78
Alkalis, carbon, loss, &c. . . . .	0.84
Insoluble in nitric acid . . . . .	1.36
	100.00

Ground amorphous phosphorus dissolves very easily in nitric acid on account of its state of sub-division.

Chlorine has no action on this variety of phosphorus unless the latter is heated, when it burns with a yellow flame.

For ignition, amorphous phosphorus requires a temperature of at least 240°.

(a) *The apparatus and process.* The conversion of yellow into amorphous phosphorus is effected by heating the former to a temperature between 240° and 250° for some time.

The apparatus employed is a cast-iron pot which is closed with a cover. A narrow tube open at both ends is screwed into the upper part of the pot. This acts as a safety valve, and avoids all risk of explosion.<sup>2</sup>

If pressure be employed within the pot and the temperature exceeds 300°, the yellow is transformed into amorphous phosphorus in a very short time. There is, however, considerable danger in this treatment which might far outweigh the economy in time. According to the method used, when the conversion is effected in open iron vessels in which the air finds but limited access, the process, though tedious, is free from all difficulty or danger.

Ordinary phosphorus may also be converted into amorphous phosphorus by chemical action, as by heating it to 200° with a small quantity of iodine.

<sup>1</sup> The hardness of amorphous phosphorus lies between calcareous spar and fluor spar.

<sup>2</sup> See Eng. Pat. 13605, by A. Albright, 1851.

(b) *The refining.* The amorphous phosphorus, obtained in the cast-iron pots, is in hard compact lumps. These are ground under water, and freed from ordinary phosphorus by boiling the ground powder with a solution of caustic soda; it is then repeatedly washed with boiling water and carefully dried by steam heat.

(c) *The packing.* The ground red phosphorus, dried in the manner described, is sent out in the dry state in tin boxes holding 10 lbs. each.

#### PROPERTIES OF ORDINARY PHOSPHORUS.

Phosphorus at the ordinary temperature is a pale yellow, soft and flexible, translucent, waxy-looking solid, which becomes hard and brittle at temperature below 5.5°. It is extremely inflammable, especially if not quite pure, and must always be kept under water. It has a great affinity for the oxygen of the air, with which it combines directly.

It also combines *directly* with chlorine, bromine, iodine, and sulphur, but not with nitrogen and hydrogen.

Phosphorus is luminous in the dark, and in a moist atmosphere a gradual oxidation takes place with formation, first of phosphorous acid, and ultimately of phosphoric acid, ozone and hydrogen peroxide being likewise produced at the same time. When exposed to daylight, under water, a whitish incrustation is formed, which frequently becomes of a reddish hue. According to Baudrimont (Compt. rend. 61, 857, 1866), the crust is formed only under influence of oxygen, and possesses all the usual properties of ordinary phosphorus. Sp.gr. at 16°, 1.82.

*Melting-point,* under water in an open vessel, 43.3°; in closed vessel without water, phosphorus melts at 30°. In both cases, if left undisturbed in a smooth glass vessel it may remain liquid at temperatures considerably below the melting-points. It distils at 269°, the vapour being colourless, and takes fire in air when heated to 34°. It is very soluble in carbon disulphide, one part dissolving 9.26 parts of phosphorus, a slight amount of heat being developed, but on cooling to ordinary temperatures some of the phosphorus is precipitated in a crystalline form.

Phosphorus is also very soluble in sulphur chloride, phosphorus trichloride, and phosphorus sulphide. It is nearly insoluble in water.

The following table shows the solubility of phosphorus in different solvents required to dissolve 1 part by weight of phosphorus. The temperature of the solvent, unless otherwise stated, is 12°:—

	Parts
Benzene (90 p.c. sp.gr. 0.878) . . . . .	82.5
Chloroform . . . . .	83
Aniline . . . . .	154
Oil of turpentine . . . . .	162
Paraffin oil (sp.gr. 0.806) . . . . .	179
Ethyl ether (sp.gr. 0.725) . . . . .	203
Olive oil . . . . .	649
Alcohol (sp.gr. 0.801) . . . . .	764
"    "    "    "    at 40° . . . . .	535
Wood spirit (sp.gr. 0.846) . . . . .	1408
"    "    "    "    at 40° . . . . .	862
Acetone . . . . .	2702
Solution of caustic soda (sp.gr. 1.35) . . . . .	194
Liquor ammonia (sp.gr. 0.880) . . . . .	3030

The ammoniacal solution becomes dark brown, and the surface of the phosphorus is coated with a brown-black deposit. When water is added to the greater number of the above solutions, the phosphorus is precipitated.

Cold concentrated nitric acid dissolves phosphorus. If exposed to the action of dilute nitric acid for some time its crystalline character becomes evident.

Sulphuric acid (92 p.c. O.V.) does not dissolve phosphorus in the cold, but attacks it on prolonged boiling. Phosphorus is insoluble in cold concentrated hydrochloric acid.

Phosphorus fumes in the air, emitting a garlic-like odour. On exposure to air, it not unfrequently melts and takes fire, and during combustion dense white fumes of phosphoric oxide are produced, which can be collected in snowy flakes. The burns produced by ignited phosphorus are of a serious nature, and are very slow in healing, any unconsumed phosphorus left on the wound being most difficult and painful to remove.

Phosphorus sometimes contains a small portion of arsenic derived from the sulphuric acid used in the preparation of the phosphoric acid. If this be present in any quantity the refined phosphorus has a red or mahogany colour. Phosphorus is a powerful poison; less than 2 grains are said to have caused death. Those who have to handle it frequently are liable to necrosis, which begins with the disintegration of the jaw-bones, and ends with their total destruction. Ill-fed and scrofulous persons are said to be specially affected. It is rather a curious circumstance that persons engaged in the manufacture of phosphorus do not appear to be affected by this disease.

Phosphorus does not conduct electricity (Faraday).

According to Deville and Troost, the vapour of phosphorus at 4.50 at 1040°; it is, therefore, that there are four atoms in the molecule.

Phosphorus is tough, and cannot be pulverised; but if melted under water and shaken until the fluid is quite cold, it is reduced to a fine state of division in the form of round pellets of various sizes; an aqueous solution of urea or alcohol aids this formation. When heated with aqueous vapour to a temperature of 250°, phosphorus decomposes the water, phosphorous acid being formed, and hydrogen being formed. When heated with water, it combines to a small extent when boiled with water.

Phosphorus *in vacuo* volatilises at ordinary temperatures. It is not luminous in pure oxygen at temperatures below 20° (Müller); but if mixed with a neutral gas, or if it be rarefied, then luminosity is at once seen (Graham). The presence of mercuric chloride and of phenol (Polstroff and Mensching, Chem. News, 57, 71), and of certain gases, such as elefant gas, sulphuretted hydrogen, or the vapours of turpentine or ether when present even in small quantities, prevent the glow of phosphorus. If hydrogen, nitrogen or carbon dioxide in which phosphorus has been exposed be brought into contact with oxygen it becomes luminous from the phosphorus diffused in the gas.

Phosphorus at 100° combines with most of the elements to form phosphides.

For example, if calcium phosphate and silica with carbon and iron (as ore or metal) be heated to a high temperature, a very fusible iron phosphide,  $\text{Fe}_3\text{P}$ , can be obtained.

Phosphorus, owing to its affinity for oxygen, is a powerful reducing agent. It precipitates copper, silver, platinum, palladium, and gold when brought into a solution of the salts of these metals.

Besides the red or amorphous, there appears to be a third allotropic modification of phosphorus—viz., metallic or rhombohedral phosphorus, which is obtained by heating the element in sealed metallic lead for some hours.

On cooling, crystals are found permeating the lead; these are separated by dilute nitric acid, which dissolves out the lead. This phosphorus is a dark crystalline substance, sp.gr. 2.34 at 15.5°.

H. M. Vernon (Phil. Mag., October 1891) states that a rhombic modification of phosphorus exists, melting at about 45.3°, and of sp.gr. 1.8272. It appears to be formed from the octahedral variety by slowly cooling it when liquid.

*Uses of phosphorus and statistics of the trade.* The chief consumption of phosphorus at present is in the manufacture of matches, in which it is used as phosphorus sesquisulphide. The so-called 'safety matches' which ignite on the box, have no phosphorus on the match itself, but have a thin layer of red or amorphous phosphorus on the sides of the box.

Phosphorus is used in medicine in small doses. It is likewise employed in form of a paste for the destruction of rats and mice. It is also used in the laboratory, and in the manufacture of many organic compounds.

Phosphorus as calcium phosphide is one of the constituents of the material used for distress signalling at sea.

Phosphor bronze, which is now extensively employed in the arts, contains a small percentage of phosphorus, which modifies the properties of copper to a large extent favourably when present in minute quantities, and unfavourably if present in more than 2-3 p.c.

At the present time, most of the phosphorus manufactured in Europe is made by Messrs. Albright and Wilson, Ltd., of Oldbury, Birmingham, England, Messrs. Coignet and Cie., Lyons, France, and the Chemische Fabrik Griesheim-Elektron, Frankfort-a-Main, Germany. There are also one or more makers in Russia, Canada and the United States of America are supplied by factories in each of those countries. J. B. R.

#### NON-METALLIC COMPOUNDS OF PHOSPHORUS.

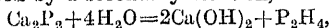
**Hydrogen phosphides.** Three of these compounds,  $\text{PH}_3$ ,  $\text{P}_2\text{H}_4$ , and  $\text{P}_3\text{H}_5$  (?), are known, the first being gaseous, the second liquid, at ordinary temperatures, and the last solid.

Phosphorus trihydride, *phosphine*,  $\text{PH}_3$ , is easily obtained by heating phosphorus with steam, or strong potash:  $\text{P} + 3\text{H}_2\text{O} = \text{PH}_3 + 3\text{H}_2\text{O}$ , or by decomposing calcium phosphide with water:  $3\text{Ca}_3\text{P}_2 + 12\text{H}_2\text{O} = 4\text{PH}_3 + \text{P}_2 + 6\text{Ca}(\text{HO})_2$ .

It is also formed by the action of dilute acids on the phosphides of zinc, iron, tin, magnesium and aluminium (Lüpké, Chem. Soc. Abstr. 1891,

397; Matignon, *Compt. rend.* 1900, 130, 1391). Hydrogen phosphide is also evolved when yellow phosphorus is acted on by warm water, by hydrogen peroxide, or by sodium hydroxide (Weyl, *Ber.* 1906, 39, 1307).

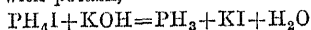
As thus prepared, the gas contains a sufficient amount of the dihydride,  $P_2H_4$ , probably produced by a secondary reaction,



to render it spontaneously inflammable. When the gas is bubbled through water, each bubble on entering the air gives rise to a vortex ring of phosphoric oxide or metaphosphoric acid. The gas also contains hydrogen produced by the gradual decomposition of the hypophosphite by the alkali:  $KH_2PO_2 + 2KOH = 2H_2 + K_2PO_4$ .

The spontaneous inflammability may be destroyed by decomposing or condensing the dihydride by exposure to light, or by passage through a tube cooled by a freezing mixture.

The trihydride may be obtained free from the dihydride by decomposing calcium phosphide with hydrochloric acid, which converts any dihydride formed into the gaseous and solid hydrides. It may be prepared pure by decomposing phosphonium iodide with water, or preferably with potash,



(Hofmann, *Ber.* 1871, 4, 200).

Very pure phosphine may readily and conveniently be prepared from a specially prepared mixture of calcium and aluminium phosphides by the action of water, the process being completed by the addition of hydrochloric acid. The only impurity in this case is a very small quantity of pure hydrogen (Matignon and Trauoy, *Compt. rend.* 1909, 148, 167).

Phosphine is a colourless gas with an offensive, garlic-like smell. Its density is 1.1829; it solidifies at  $-133.5^\circ$  (Olzewski) and has the critical temperature  $52.8^\circ$  and the critical pressure 64 atmospheres.

It may be mixed with oxygen, but if the pressure of the mixture be suddenly diminished, an explosion occurs. (Compare also Lemoult, *Compt. rend.* 1907, 145, 374). The gas also takes fire when brought into contact with dilute nitric acid or if mixed with the vapours of chlorine or bromine water and is decomposed into hydrogen and phosphorus by sparks. Phosphine is a very poisonous gas, a small quantity, when breathed, producing in turn dyspnoea and death.

It is somewhat soluble in water and is absorbed by copper sulphate and mercuric chloride and bromide, forming compounds of the metals, and in some cases salts (Joannis, *Compt. rend.* 1899, 128, 1322, 1398; 129, 336; Rubénovitch, *ibid.* 1898, 127, 270; 1899, 128, 1398; Ribeau, *ibid.* 128, 1452; Lemoult, *ibid.* 1907, 145, 1175).

Like ammonia, it also combines with metallic chlorides such as those of tin, antimony, aluminium, &c., and with hydrobromic and hydroiodic acids to form phosphonium compounds, of which phosphonium iodide,  $PH_4I$ , is used as a powerful reducing agent and in the preparation of many organic phosphorus compounds.

Gattermann and Hausknecht (*Ber.* 1890,

1174) employ the following process for preparing the dihydride. A large three-necked Woulff's bottle, three-quarters filled with water, is freed from air by a current of hydrogen supplied through a tube fitted in one neck and dipping just beneath the water, and is heated in a water-bath to  $60^\circ$ . Carbon disulphide is then introduced in lumps.

50 grams through a wide, funnel-topped tube fitted to the second neck and just dipping beneath the water. The evolved gases pass through a tube fitted to the third neck to a test-tube, from which passes a tube to a condensing-tube surrounded by iced water. The water in the gas condenses in the test-tube, and the hydride,  $P_2H_4$ , liquefies in the condenser, about 2 c.c. being obtained from 50 grams of calcium phosphide. The undensified gas may be passed through a flask containing hydrochloric acid, which decomposes the remaining  $P_2H_4$  into the trihydride and the solid hydride.

The dihydride is a colourless liquid of sp-gr. 1.007 at  $12^\circ$ , boiling, when not too suddenly heated, at  $57^\circ-58^\circ$  ( $735$  mm.) (Gattermann and Hausknecht, *l.c.*). On exposure to light, or under the action of hydrochloric acid, it decomposes into the trihydride and the solid hydride. Small quantities of the dihydride impart spontaneous inflammability to hydrogen, carbon monoxide, and other combustible gases.

The solid hydride is obtained, as above, as a yellow powder, by decomposing the dihydride with hydrochloric acid, or by the action of light, or by treating calcium phosphide with hot hydrochloric acid, or by treating calcium phosphide with water and allowing the gas formed to come in contact with calcium chloride (Stock, Böttcher and Lenger, *Ber.* 1909, 42, 2839). It ignites when heated in the air.

After exposure to the air, it acquires an acid reaction and the odour of phosphine. It is quite stable in the dark, but in sunlight it becomes red and evolves an inflammable gas. In a vacuum it evolves pure phosphine, and this is recommended as a method of preparing the latter by Stock, Böttcher and Lenger (*l.c.*). The red substance which remains behind is, according to these authors,  $P_3H_2$ , produced thus,  $6P_2H_4 = 6P_3H_2 + 6PH_3$ . The hydride  $P_3H_2$  is stable in dry air, but in moist air it decomposes forming phosphine and phosphoric acid. It dissolves in liquid ammonia forming a black compound varying in composition between  $P_3H_2 \cdot NH_3$  and  $2P_3H_2 \cdot NH_3$ .

Similar black compounds are produced by the union of the solid hydride  $P_2H_4$  with ammonia and piperidine (Schenck, *Ber.* 1903, 36, 4202; Stock, *ibid.* 1903, 36, 1120; Stock, Böttcher and Lenger, *l.c.*).

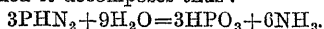
#### Compounds of Phosphorus and Nitrogen.

A considerable number of these compounds exists.

Phosphorus nitride  $P_3N_5$  can be obtained and absolutely pure by saturating pentasulphide with pure dry ammonia at the ordinary temperature, subsequently heating the products in an atmosphere of hydrogen, then in a current of ammonia at  $850^\circ$  (Stock and Hoffmann, *Ber.* 1903, 36, 314; Stock and Grüneberg, *ibid.* 1907, 40, 2573;

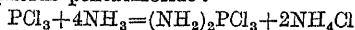
Stock and Johannsen, *ibid.* 1908, 41, 1593). It varies in colour from pure white to dark red, according to the time of heating in its preparation and has sp.gr. of 2.51 at 18°. At the ordinary temperature it is inactive, but acts as a powerful reducing agent at a high temperature. It is decomposed by many metals and by water at 180°. When heated in chlorine or oxygen it takes fire.

**Phospham**  $\text{PN}_2\text{H}(\text{?})$  is obtained as an amorphous, light, white powder, insoluble in water and infusible at a red heat, when the product of the reaction of ammonia on phosphorus pentachloride is heated in the absence of air until fumes of ammonium chloride cease to be evolved (Besson, *Compt. rend.* 1892, 114, 1264; Besson and Rosset, *ibid.* 1908, 146, 1149). When dry, it is oxidised by heating in air, evolving white fumes; if previously moistened it decomposes thus:

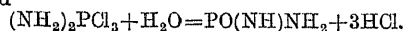


**Phosphoramidate**  $\text{P}(\text{NH}_2)_3$  is obtained by the action of ammonia on phosphorus tribromide or triiodide at  $-70^\circ$  (Hugot, *Compt. rend.* 141, 1235). It is an unstable yellow solid which readily decomposes at  $0^\circ$ , forming phosphorimide,  $\text{P}_2(\text{NH})_2$ , a brown solid which decomposes on heating into ammonia and phosphorus (v. also Stock, *Ber.* 1908, 41, 1593).

**Phosphamide (phosphodiamide)**  $\text{PO}(\text{NH})\text{NH}_2$  is a white powder obtained by the action of water on the product of the action of ammonia on phosphorus pentachloride:



and



**Phosphoryl triamide (phosphotriamide)**  $\text{PO}(\text{NH}_2)_3$  is a white amorphous powder obtained by the action of dry ammonia on phosphorus oxychloride (Schiff, *Zeitsch. öffentl. Chem.* 5, 609).

**Phosphorus diamide**  $\text{POH}(\text{NH}_2)_2$  is obtained by the action of ammonia on a solution of phosphorus oxide in ether or benzene. It is a white powder which dissolves in water with incandescence and is violently decomposed by dilute hydrochloric acid, forming phosphine, phosphoric acid, and ammonium chloride and ammonium phosphate (Tutton, *Chem. Soc. Trans.* 1881, 10, 100).

**Phosphamidic acid or amidophosphoric acid**  $\text{PO}(\text{NH}_2)(\text{OH})_2$  is formed by the action of dry ammonia on phosphorus pentoxide (Biltz, *Ber.* 1894, 27, 1257); or the potassium salt of the acid is obtained by the action of potassium hydroxide on the corresponding phenyl ester, the free acid being formed by the decomposition of the lead or silver salt by sulphuretted hydrogen and precipitating it from the filtrate with alcohol (Stokes, *Amer. Chem. J.* 1893, 15, 198; 16, 154). It forms colourless microscopic crystals having a sweet taste and forming both normal and acid salts.

**Diamidophosphoric acid**  $\text{PO}(\text{NH}_2)_2\text{OH}$ , is a crystalline compound obtained in the same way as the foregoing acid (Stokes, *Ber.* 1894, 27, 565). It forms the silver salts  $(\text{NH}_2)_2\text{PO} \cdot \text{OAg}$  and  $(\text{NHAg})_2\text{P}(\text{OAg})_3$ .

A number of imido phosphoric acids have also been prepared (Stokes, *Amer. Chem. J.* 1896, 18, 629; 1898, 20, 740).

**Phosphoryl nitride (phosphomonamide)**  $\text{PON}$  is obtained when phosphorus is heated to redness out of contact with air. Several phosphamic acids, and amides containing chlorine, are also known (v. Gladstone, *Chem. Soc. Trans.* 1864, 225; 1865, 1; 1866, 1 and 290; Salzmänn, *Ber.* 1874, 7, 494; Winter, *J. Amer. Chem. Soc.* 1904, 26, 1484; Stokes, *Amer. Chem. J.* 19, 782).

#### Compounds of phosphorus and sulphur.

Several liquid and solid sulphides, all of which are very inflammable and more fusible than either of the constituent elements, are known. The liquids  $\text{SP}_4$  and  $\text{SP}_2$  are not compounds but only solutions of sulphur in phosphorus (Boulouch, *Compt. rend.* 1902, 135, 165; Stock and Bezhold, *Ber.* 1908, 41, 657; Stock, *ibid.* 1909, 42, 2062). The solid sulphides,  $\text{P}_4\text{S}_3$ ,  $\text{P}_3\text{S}_2$ , and  $\text{P}_2\text{S}_5$  are obtained by carefully heating sulphur with amorphous phosphorus. The composition  $\text{P}_3\text{S}_8$  (Dupré) or  $\text{P}_3\text{S}_{12}$  (Berzelius, *Gmelin's Handb.* 2, 218) has been assigned to a body obtained in rhombic sulphur-like crystals by solution of sulphur in sulphur diphosphide. According to Ramme (*Ber.* 1879, 12, 940, 1350), the crystals are merely sulphur containing phosphorus (cf. Boulouch, *Compt. rend.* 1906, 143, 41).

**Phosphorus pentasulphide**  $\text{P}_2\text{S}_5$ , which is employed in the preparation of organic sulphur compounds, is produced by gently heating a mixture of excess of powdered roll sulphur and amorphous phosphorus. A small portion of the mixture is first heated in a stream of carbon dioxide until reaction sets in. The source of heat is then removed and the rest of the mixture is added in small quantities. After cooling, the mass is extracted with carbon disulphide (Stock and Scharfenberg, *ibid.* 1908, 41, 558).

The product forms a greyish-yellow crystalline mass, which may be obtained in transparent crystals by sublimation. According to Stock and Thiel (*Ber.* 1905, 38, 277), the sulphide exists in at least two forms.

The ordinary compound melts at  $274^\circ$ – $276^\circ$  (Meyer, *ibid.* 1879, 12, 610), and boils at  $519^\circ$  at 734 mm. pressure (Goldschmidt, *ibid.* 1882, 15, 304). The other modification melts at about  $255^\circ$ , is more soluble in carbon disulphide and can be obtained by the distillation of the ordinary sulphide *in vacuo* and rapidly cooling the product (Stock and Scharfenberg, *l.c.*).

Phosphorus pentasulphide dissolves in liquid ammonia forming ammonia thioimaphosphoric compounds from which imidophosphoric acid has been obtained (Stock, *Ber.* 1906, 39, 1967).

**Phosphorus sesquisulphide**  $\text{P}_4\text{S}_3$  forms rhombic prisms, m.p.  $166^\circ$ , b.p.  $380^\circ$ . It is easily inflammable and is slowly decomposed by boiling water forming sulphuretted hydrogen, phosphine, and phosphorous acid (Clayton, *Chem. Soc. Proc.* 1902, 129; *ibid.* 1903, 231; Mai and Scheffer, *Ber.* 1903, 36, 870). The commercial product sometimes contains free phosphorus, the presence of which can be detected by passing a current of hydrogen over the sulphide when, if phosphorus is present, the issuing gas will burn with a green flame.

In carbon disulphide solution, phosphorus

sesquisulphide absorbs iodine forming  $P_4S_3I_2$ , orange-yellow crystals, m.p.  $119.5^\circ$ —this compound can be used as a means of detecting the sesquisulphide (Walter, Chem. Zeit. 1907, 31, 640). According to Gartenmeister (J. Soc. Chem. Ind. 1908, 837), easily inflammable but not explosive substances which are not sensitive to moisture can be obtained by heating together various proportions of red phosphorus, sulphur, and the sulphides of metals such as antimony, to about  $170^\circ$ .

**Phosphorus sulphoxides**  $P_4O_6S_4$ , m.p.  $102^\circ$ , b.p.  $295^\circ$ , and  $P_2O_5S_3$ , which decomposes at  $200^\circ$ , forming phosphorus pentoxide and pentasulphide, have been prepared by Thorpe and Tutton (Chem. Soc. Trans. 1891, 1024), and Besson (Compt. rend. 1897, 124, 151).

For other work on phosphorus sulphides, v. Rebs (Annalen, 1888, 246, 356), Dervin (Bull. Soc. chim. 41, 433), Isambert (Compt. rend. 1883, 96, 1499, 1771), Lemoine (*ibid.* 1630), Schulze (Ber. 1883, 16, 2066), Frouin (Chem. Zeit. Rep. 1899, 23, 213), Weelwright (J. Soc. Chem. Ind. 1903, 229), Boulouch (Compt. rend. 1904, 138, 363; 1906, 142, 1045; 143, 41), Dervin (*ibid.* 138, 366), Girvan (*ibid.* 142, 398), Stock (Ber. 1909, 42, 2062).

#### Compounds of phosphorus and selenium.

Phosphorus and selenium can be fused together in all proportions, a red mass being formed; the only definite compounds, however, are  $P_4Se_3$ ,  $P_2Se_5$ , and possibly  $P_2Se_3$ . These compounds are decomposed by moist air, and when treated with alkalis or alkali sulphides yield complex salts such as potassium thio-phosphates  $2K_2S.P_2Se_3.5H_2O$  (v. Berzelius, *ibid.* 2, 242; Bogen, Annalen, 1862, 124, 57; Hahn, J. pr. Chem. [i.] 93, 430; Muthmann and Clever, Zeitsch. anorg. Chem. 1896, 13, 191; Meyer, *ibid.* 1902, 30, 258).

#### Haloid compounds of phosphorus.

**Phosphorus trichloride**  $PCl_3$ , may be prepared by passing dry chlorine over heated amorphous phosphorus, or over dry ordinary phosphorus, which takes a few weeks to convert into pentachloride which may have been formed into the trichloride (Dumas, Ann. Chim. Phys. [iii.] 55, 172). It is a mobile, colourless, fuming liquid of pungent smell, boiling at  $75.95^\circ$  (760 mm.), and having a sp.gr. of  $1.61275_{40}^{0^\circ}$  (Thorpe, Proc. Roy. Soc. 24, 295). It absorbs water with production of hydrochloric acid and phosphorous acids and a white solid phosphorus oxychloride,  $POCl_3$  (Compt. rend. 1898, 125, 771). It dissolves in benzene and is itself soluble in benzene. When mixed with alcohol, heat is evolved, with production of ethyl chloride and phosphorous acid, and evolution of hydrochloric acid. Phosphorous ester is also produced (Béchamp, Compt. rend. 1855, 40, 944; 41, 23). It also unites with ammonia forming additive compounds (Besson, *ibid.* 1890, 111, 972).

Phosphorus trichloride reacts with glycerol and with glycol, yielding in the former case phosphorous esters of glycerol and of monochlorhydrin which are decomposed by water

forming the compounds  $P_2(OH)_4O_2.C_3H_7OH$  and  $P(OH)_2O.C_3H_7OH.HCl$  of which the calcium derivatives have been isolated (Carré, Compt. rend. 1903, 136, 1456).

**Phosphorus pentachloride**  $PCl_5$  may be obtained by passing dry chlorine over the well-cooled trichloride until the whole is dry, or by the action of excess of chlorine on phosphorus. On the large scale, it is best prepared by passing excess of dry chlorine through a cooled solution of phosphorus in carbon disulphide, and finally crystallising out the product. It forms white lustrous crystals of unpleasant smell, volatilising below  $100^\circ$  without liquefying. Under pressure, it melts at  $148^\circ$  (Strecker). The vapour decomposes, when heated, into the trichloride and chlorine (Wanklyn and Robinson, Proc. Roy. Soc. 12, 507; Wegscheider, Monatsh. 1899, 20, 307).

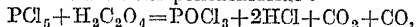
In moist air, the pentachloride is converted into the oxychloride  $POCl_3$  and  $HCl$ . Hydrochloric acid converts it into the oxychloride and a solution of sulphuryl chloride  $SO_2Cl_2$  into  $POCl_3$  and  $SO_2$ . Phosphorus pentachloride is much used in the preparation of phosphorus chlorides. It forms chlorides of many elements or an additive compound with ammonia, and the temperature of the reaction is  $100^\circ$  (Compt. rend. l.c.).

Both chlorides form additive compounds with certain chlorides and bromides such as  $PCl_3.2BBr_3$ ;  $PCl_5.2BBr_3$ , &c. (Taribile, Compt. rend. 1901, 132, 83; Strecker and Schurigin, Ber. 1909, 42, 1767).

**Phosphorus chlorobromide**  $PCl_3Br_2$  is obtained by the action of bromine on phosphorus trichloride. It solidifies at  $-20^\circ$ , and decomposes when heated to  $35^\circ$  (Michaelis, Ber. 1872, 5, 9). It combines with various proportions of bromine (v. Michaelis, l.c.; Prinvalet, Compt. rend. 1872, 74, 868; and Stern, Chem. Soc. Trans. 1886, 815).

**Phosphorus chloro-iodide**  $PCl_3I_2$  is said to be obtained in fine red hexagonal crystals by the action of iodine on phosphorus trichloride (Moot, Ber. 1879, 13, 2029).

**Phosphoryl chloride** (phosphorus oxychloride)  $POCl_3$  may be prepared by heating dry oxide or boric acid with the pentachloride:



or by heating the pentachloride with the pentoxide in a sealed tube:  $3PCl_5 + P_2O_5 = 5POCl_3$ . It can be conveniently prepared by the action of potassium chlorate on phosphorus trichloride (Dervin, Compt. rend. 1883, 97, 576; Ullmann and Fornaro, Ber. 1901, 34, 2172); or, according to Erdmann (Zeitsch. angew. Chem. 1903, 89), by passing a current of dry chlorine over a strongly heated, powdered mixture of carbon and a metaphosphate.

Phosphoryl chloride is a colourless, fuming liquid, boiling at  $107.23^\circ$  (760 mm.), and having a sp.gr. of  $1.71163_{40}^{0^\circ}$  (Thorpe, Chem. Soc. Trans. 37, 338). When cooled it solidifies to crystals which melt at  $-1.5^\circ$  (Geuther and Michaelis, Ber. 1871, 4, 769). Its molecular depression of the freezing-point is  $0.48^\circ$  (Huntley, Chem. Soc. Trans. 1891, 205). Water rapidly decomposes it into hydrochloric and phosphoric acids. It forms crystalline double compounds with many metallic chlorides.



**Metaphosphoryl chloride (?)**  $\text{PO}_2\text{Cl}$ . A straw-coloured viscous body obtained, together with phosphoryl chloride, by the action of chlorine on cooled phosphorous oxide (Thorpe and Tutton, Chem. Soc. Trans. 1890, 572); has been found to possess a composition corresponding with the formula  $\text{PO}_2\text{Cl}$ . It has, however, been shown by Huntley (*ibid.* 1891, 202) that this body consists of at least two substances, one of which is pyrophosphoryl chloride, whilst the other is a compound or mixture of the composition  $\text{P}_2\text{O}_5\text{Cl}_5$ .

According to Besson (Compt. rend. 1897, 124, 1099), metaphosphoryl chloride is obtained by the action of a small amount of water on phosphoryl chloride.

**Pyrophosphoryl chloride**  $\text{P}_2\text{O}_5\text{Cl}_4$  is a colourless, fuming liquid, boiling between  $210^\circ$ – $215^\circ$ . It is obtained by the action of nitrogen peroxide on cooled phosphorus trichloride. Nitrosyl chloride is evolved, and pyrophosphoryl chloride remains, together with phosphorus pentoxide, phosphorus trichloride, and phosphoryl chloride, from which it is separated by fractional distillation (Geuther and Michaelis, Ber. 1871, 4, 767). It is also obtained as stated above or by the action of water on phosphorus pentachloride or by treating the pentachloride (6 parts) with the pentoxide (1 part) (Oddo, Gazz. chim. ital. 1899, [ii.] 29, 330).

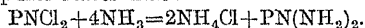
**Phosphoryl bromodichloride**  $\text{POBrCl}_2$  (v. Menshutkin, J. pr. Chem. [i.] 98, 485; Besson, Compt. rend. 1896, 122, 814), is a highly refractive liquid, boiling at  $135^\circ$ – $138^\circ$  (760 mm.), and having a sp.gr. of  $2.12065_{40}^\circ$  (Thorpe, Chem. Soc. Trans. 37, 344). When cooled, it solidifies in tables, which melt at  $11^\circ$  (Geuther and Michaelis, Ber. 1871, 4, 769;  $13^\circ$  (Besson, *l.c.*).

By the action of hydrogen bromide on phosphoryl chloride at  $400^\circ$ – $500^\circ$ , it is obtained together with phosphoryl dibromochloride  $\text{POBr}_2\text{Cl}$ , which melts at  $30^\circ$  and has b.p.  $165^\circ$  (Besson, *l.c.*).

**Thiophosphoryl chloride**  $\text{PSCl}_3$ , is a colourless, fuming liquid, produced by the action of sulphuretted hydrogen on the pentachloride, or, better, by heating a mixture of phosphorus pentasulphide and pentachloride. It boils at  $125^\circ$  (760 mm.), and has a sp.gr. of  $1.6682_{40}^\circ$  (Thorpe, Chem. Soc. Trans. 37, 341).

**Nitrogen chlorophosphide**  $\text{PNCl}_2$  is obtained by gently heating a mixture of phosphorus pentachloride and ammonium chloride (white precipitate) or ammonium chloride (Stokes, Ber. 1895, 28, 437; Amer. Chem. J. 1896, 18, 629, 780; *ibid.* 1897, 19, 782; *ibid.* 1898, 20, 740; Besson, Compt. rend. 1892, 114, 1264, 1479; Besson and Rossett, *ibid.* 1900, 143, 37). It sublimes in rhombic prisms, melting at  $110^\circ$ , and boiling at  $240^\circ$  (v. Gladstone and Holmes, Chem. Soc. Trans. 17, 225).

With liquid ammonia, nitrogen chlorophosphide reacts thus:



The compound  $\text{PN}_3\text{H}_4$  is a white substance soluble in water, and on heating to  $222^\circ$  loses ammonia and is converted into phospham. Nitrogen chlorophosphide in carbon tetrachloride solution, when treated with dry ammonia gas, yields slender silky needles of the

compound,  $\text{P}_2\text{N}_3\text{H}_2\text{Cl}_2$ , together with some  $\text{PN}_3\text{H}_4$  (Besson, Compt. rend. 1908, 146, 1149).

A number of nitrogen compounds corresponding with the  $(\text{PNCl}_2)_n$ , have been obtained.

**Phosphorus tribromide**  $\text{PBr}_3$  is best prepared by slowly dropping bromine on to excess of amorphous phosphorus in a flask fitted with an inverted condenser, or by dropping bromine on to ordinary phosphorus covered by a layer of benzene (Christomanos, Ber. 1904, 37, 2883). The rectified product is a colourless mobile liquid of strong, pungent smell, boiling at  $172.9^\circ$  (760 mm.), and solidifying at  $-41.5^\circ$ , and having a sp.gr. of  $2.923_{40}^\circ$  (Thorpe, Chem. Soc. Trans. 37, 335). It acts as a reducing agent on many organic compounds, and forms double salts of the type  $\text{CuBr}_2 \cdot \text{PBr}_3$  (Arbusoff, J. Russ. Phys. Chem. Soc. 1906, 38, 293).

**Phosphorus pentabromide**  $\text{PBr}_5$  is produced by the addition of bromine to the cooled tribromide; it forms yellow crystals of pungent smell, melting to a red liquid, which decomposes into the tribromide and bromine at  $100^\circ$ . According to Castle and Beaty (Amer. Chem. J. 1899, 21, 322; *ibid.* 1900, 23, 505), when the pentabromide is mixed with bromine and sublimed, red prisms of a *heptabromide*,  $\text{PBr}_7$ , are formed.

**Phosphorus trifluorodibromide**  $\text{PF}_2\text{Br}_2$  has also been obtained.

**Phosphoryl bromide** (or *phosphorus bromide*)  $\text{POBr}_2$  occurs in flat crystals, melting at  $45^\circ$ – $46^\circ$  and boiling at  $195^\circ$  (760 mm.), and is prepared similarly to phosphoryl chloride.

According to Berger (Compt. rend. 1908, 146, 400), it forms colourless crystals, m.p.  $55^\circ$ – $56^\circ$ , b.p.  $189.5^\circ$  (774 mm.).

**Phosphonium bromide**  $\text{PH}_4\text{Br}$  crystallises in colourless cubes, b.p.  $30^\circ$  and resembles the iodine compound.

**Thiophosphoryl bromide**  $\text{PSBr}_3$ , a yellow, crystalline body, m.p.  $38^\circ$ , and *tribromide*  $\text{P}_2\text{S}_3\text{Br}_4$ , a fuming liquid, and *metathiophosphoryl bromide*  $\text{PS}_2\text{Br}$ , are also known.

Bromo-chloro-thio compounds of phosphorus have been prepared by Besson (Compt. rend. 1896, 122, 1057).

**Phosphorus di-iodide**  $\text{P}_2\text{I}_4$  is prepared by the gradual addition of 8.2 parts of iodine to a solution of 1 part of phosphorus in carbon disulphide. On distilling off the disulphide, or on cooling it, the iodide remains or crystallises out in bright orange-yellow crystals which fuse at about  $110^\circ$  (Corenwinder, Ann. Chim. Phys. [iii.] 30, 242).

A rapid and safe method of producing phosphorus di-iodide is described by Doughty (J. Amer. Chem. Soc. 1905, 27, 1444); 50 grams of iodine and 4 grams of red phosphorus are heated in a 200 c.c. flask over a free flame until melted. After cooling to  $60^\circ$ , 2.5 grams of yellow phosphorus are added in small pieces.

When dry iodine is added to a solution of phosphorus in dry carbon disulphide, in quantity less than that necessary to convert the phosphorus into the di-iodide and the mixture is exposed to sunlight, *phosphorus subiodide*,  $\text{P}_4\text{I}$ , separates.

It is an amorphous, red powder which decomposes without melting and is decomposed by most reagents (Boulough, *Compt. rend.* 1905, 141, 256).

**Phosphorus tri-iodide**  $PI_3$  is prepared similarly to the di-iodide, but with the use of a correspondingly larger proportion of iodine. It forms red six-sided deliquescent prisms, m.p.  $61^\circ$  (Corenwinder, *l.c.*, Snape, *Chem. News*, 1896, 74, 27; Besson, *Compt. rend.* 1897, 124, 1346).

**Phosphonium iodide**  $PH_4I$  is obtained by the union of phosphine with hydriodic acid, or by the action of water and iodine on excess of phosphorus.

The iodine and phosphorus are preferably combined in carbon disulphide, which is then distilled off and the water added gradually during passage of carbon dioxide (Hofmann, *Ber.* 1873, 6, 291). The iodide is thus obtained as a sublimate of glistening deliquescent quadratic prisms, b.p. about  $80^\circ$  but readily vapourising at a lower temperature, decomposed by water into hydriodic acid and phosphine. It is a powerful reducing agent, and is employed as such in the preparation of many organic compounds.

**Phosphorus triiodide**,  $P_2SI_2$ , m.p.  $75^\circ$  (Besson, *Compt. rend.* 1896, 122, 1057), and  $P_2S_2I_2$  (Ouvrard, *ibid.* 1892, 115, 1301) also exist.

**Phosphorus trifluoride**  $PF_3$  may be prepared by carefully heating dry copper phosphide with lead fluoride, or by allowing arsenic trifluoride to drop upon phosphorus trichloride, or, preferably, by gently warming a mixture of dry zinc fluoride and phosphorus tribromide. It is a colourless, non-volatile gas, which condenses at  $-10^\circ$  and solidifies at  $-40^\circ$  under a pressure of 40 atmospheres to a colourless solid, b.p.  $-15^\circ$ , m.p.  $-100^\circ$ , melting at  $-100^\circ$ . It dissolves slowly in water. It produces silicon fluoride, with separation of phosphorus, when heated in contact with glass. It combines directly with bromine, giving an amber-coloured mobile liquid having the composition  $PF_3Br_2$  (Moissan, *Compt. rend.* 1884, 99, 655, 970; 1885, 100, 272, 1348; *Ann. Chim. Phys.* [vi.] 19, 286).

**Phosphorus pentafluoride**  $PF_5$  is obtained by the action of arsenic trifluoride on phosphorus pentachloride (Thorpe, *Proc. Roy. Soc.* 1876, 122). It is a heavy, fuming, colourless, unflammable gas, which is rapidly decomposed by water into hydrofluoric acid and phosphoric acid. It combines with dry ammonia to produce a white solid  $2PF_5 \cdot 5NH_3$ , and, according to Tassel (*Compt. rend.* 1890, 110, 1264), combines with nitrogen peroxide to produce a white crystalline compound of the composition  $PF_5 \cdot NO_2$ ; v. also Moissan (*ibid.* 1885, 101, 1490; 1886, 103, 1257). It condenses to a liquid, b.p.  $-75^\circ$  and solidifies to a flocculent mass at  $-83^\circ$  (Moissan, *ibid.* 1904, 138, 789).

**Phosphoryl fluoride, phosphorus oxyfluoride**  $POF_3$  may be prepared by the action of the electric spark on a mixture of phosphorus trifluoride and oxygen, by the action of phosphorus pentachloride on phosphorus trifluoride, or by gently warming zinc fluoride with phosphorus pentachloride (*Compt. rend.* 1886, 102, 1245; *Bull. Soc. Chim.* [iii.] 5, 458), or, better, by the action of phosphorus pentachloride on phosphorus trifluoride by Thomsen (*Chem. Soc. Trans.* 1889, 793), or by gently heating a mixture of cryolite and phosphorus

pentoxide. It is a colourless, fuming gas, rapidly absorbed by water, and without action, when dry, on glass or mercury. It condenses to a liquid which boils at  $-40^\circ$  and solidifies to a crystalline mass at  $-68^\circ$  (Moissan, *l.c.*).

**Thiophosphoryl fluoride**  $PSF_3$  may be obtained by heating a mixture of arsenic trifluoride and phosphorus thiochloride in a sealed glass tube to  $150^\circ$ , or by heating a mixture of amorphous phosphorus, sulphur, and lead or bismuth fluoride, or, preferably, by heating a mixture of powdered, freshly-fused lead fluoride, and freshly-made phosphorus pentasulphide in a leaden tube from which air has been expelled by a current of dry nitrogen:  $P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3$ . The action commences at  $170^\circ$ , and the temperature should be kept below  $250^\circ$ . The gas is stored over mercury in a glass holder containing fragments of quicklime, which gradually absorb the phosphorus trifluoride and any trace of silicon fluoride contained in the gas. The quicklime should be freed from air before use by repeatedly passing dry nitrogen into the holder and exhausting with a Sprengel pump. At ordinary temperatures, thiophosphoryl fluoride is a heavy colourless gas which condenses at a pressure of 10 to 11 atmospheres to a colourless liquid. A jet of the gas burns spontaneously with a greyish-green flame of extremely low heating power. If a considerable quantity of the gas be suddenly exposed to the air, a fine blue flash, followed by the greyish-green flame, is observed. The gas burns spontaneously with a yellow flame in oxygen, but the dry gas does not inflame in dry oxygen in presence of sufficient of its oxidation products. The mixture instantly inflames on exposure to air or on introduction of moisture.

When heated or exposed to the electric spark, the gas decomposes into sulphur, phosphorus, and silicon fluoride. It is without action on mercury, sulphuric acid, carbon disulphide, or benzene. It dissolves to some extent in ether, the solution burning with a greenish flame. It dissolves slowly with decomposition in water and solution of potash, soda, or ammonia. It combines with ammonia gas to form a white solid. Gently heated sodium burns with a red flame in the gas, the residue evolving spontaneously inflammable phosphine when treated with water. When heated in a glass tube the gas deposits phosphorus and sulphur, with formation of silicon tetrafluoride, which occupies three-fourths of the volume of the original gas:  $4PSF_3 + 3Si = 3SiF_4 + P_4 + S_8$  (Moissan, *Chem. Soc. Trans.* 1888, 793; 1889, 794).

#### Oxides and acids of phosphorus.

The product of the combustion of phosphorus in a limited supply of air consists of a mixture of the four oxides  $P_4O_6$ ,  $P_4O_8$ ,  $P_2O_5$ , and  $P_4O_{10}$ .

The first of these oxides,  $P_4O_6$ , was obtained by Le Verrier (*Annalen*, 1838, 27, 167), but whilst its existence has been maintained by some chemists, this is denied by many others (Michaelis and Pitsch, *ibid.* 1899, 310, 45; Michaelis and Arend, *ibid.* 1900, 314, 259; 1902, 325, 361; Biltz, *Ber.* 1894, 27, 1257; Besson, *Compt. rend.* 1897, 124, 763; 1897, 125, 1032; 1901, 132, 1556; Chapman and Libury, *Chem. Soc. Trans.* 1899, 973; Burgess and Chapman, *ibid.* 1901, 1235; Browning, *Chem. Soc. Proc.*

1901, 243; Jungfleisch, *Compt. rend.* 1907, 145, 325).

**Phosphorous oxide, phosphorous anhydride**  $P_2O_5$ . The existence of this compound as one of the products of the slow combustion of phosphorus seems to have been first noticed by Sage in 1777. It appears also to have been obtained by Cabell as a sublimate from the mixed oxides (*Chem. News*, 50, 209). It, however, received no systematic examination until Thorpe and Tutton (*Chem. Soc. Trans.* 1890, 545; 1891, 1019) obtained it in a state of purity by the following method:—

Pieces of dried phosphorus are placed in a glass tube drawn out, but open at one end, and connected at the other end with a brass tube surrounded by a tube filled with water. The inner tube is connected with a long-limbed U-tube fitted at the bend with a branch leading to a small bottle, into which the product of the action may be passed by warming the limbs of the U-tube. A freezing mixture surrounds the U-tube and bottle.

The phosphorus having been ignited by heating the tube, is oxidised by drawing air through the apparatus with an aspirator, and after about 15 minutes, the water around the brass tube is heated to about  $50^\circ$ , as indicated by a thermometer fitted to the outer tube, and the temperature is maintained thereabouts until near the end of the operation, when it is raised to about  $60^\circ$ . The readily fusible trioxide gradually passes over from the combustion products in the brass tube and solidifies in the U-tube, a loose plug of glass wool in the brass tube preventing the escape of the other oxides. The product is obtained in about four-fifths of the weight of the phosphorus burned, in order to obtain a pure product.

The product solidifies in the U-tube as a snow-white waxy mass. It may also be obtained in long feathery aggregations or in thin isolated prisms, terminated by pyramids, and probably belonging to the monoclinic system, as do those of the corresponding compound with arsenic or antimony.

It is a white, crystalline solid (l.c.), a continuous mass of crystals of phosphorous oxide can be obtained by oxidising pure dry phosphorus at a low temperature at 18–20 mm. pressure.

Phosphorous oxide possesses a peculiar phosphorus-like smell. It fuses at  $22.5^\circ$  to a mobile liquid, sp.gr. 1.9358  $\frac{24.8^\circ}{4^\circ}$ , which normally re-solidifies at  $21^\circ$ , but which sometimes exhibits the property of superfusion. It boils at  $173.1^\circ$  (760 mm.). When heated in a sealed tube to about  $210^\circ$  the oxide becomes turbid, and at  $440^\circ$  is entirely decomposed into the tetroxide and amorphous phosphorus.

Phosphorous oxide is slowly dissolved by cold water, forming phosphorous acid. With hot water the action is violent, large quantities of the red suboxide or amorphous phosphorus being produced, with evolution of spontaneously inflammable phosphine.

It is insoluble in ether, and dissolves unchanged in benzene, or chloroform, but is instantly ignited in contact with absolute alcohol. When this action is properly controlled, *di-ethyl phosphorous acid* is obtained.

The oxide is spontaneously oxidised in presence of air or oxygen. When thrown into oxygen heated at  $50^\circ$  or  $60^\circ$ , it ignites with great brilliancy. It inflames readily when exposed to the air, especially when warmed or when in contact with fabrics or paper. When thrown into chlorine, it burns with a greenish flame. The slow action of chlorine on the cooled oxide gives a mixture of phosphoryl chloride and the so-called metaphosphoryl chloride.

Bromine acts in a similar manner, but with previous formation of phosphorus pentabromide. With iodine it forms the phosphorus pentoxide:  $5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5$ . Heated with sulphur it yields phosphorus sulphoxide  $P_4O_6S_4$ , forming clear transparent crystals, m.p.  $102^\circ$  and b.p.  $295^\circ$ , deliquescent rapidly in the air, and readily dissolved by water, forming sulphuretted hydrogen and phosphoric acid:  $P_4O_6S_4 + 10H_2O = 4H_3PO_4 + 2H_2S$  and Tutton, *Chem. Soc. Trans.* 1890, 545.

Vapour density determinations show that the gaseous molecule of the oxide has the formula  $P_2O_5$ . Determinations of the molecular weight by Raoult's method give similar results.

**Phosphorus tetroxide**  $P_2O_4$  was first obtained by Thorpe and Tutton (*Chem. Soc. Trans.* 1886, 833) by heating the mixed oxides obtained by the slow combustion of phosphorus in a sealed exhausted tube at about  $290^\circ$ . A sublimate of this oxide in clear, transparent, colourless, orthorhombic crystals, m.p.  $180^\circ$ , is thus obtained. It may be prepared, together with amorphous phosphorus, by heating phosphorus in a sealed tube to about  $440^\circ$ .

The tetroxide is deliquescent and dissolves in water, with evolution of heat, the strongly acid solution being unchanged on boiling. The solution reduces mercuric chloride to calomel on warming, and gives a white precipitate, which rapidly blackens with silver nitrate. Its vapour density at  $1400^\circ$  is 230 (West, *Chem. Soc. Trans.* 1902, 933).

**Phosphorus pentoxide, phosphoric oxide, phosphoric anhydride**  $P_2O_5$  may be obtained in a state of purity by heating a porcelain dish, containing burning phosphorus, in a three-necked globe, and drawing dried air through the globe with an aspirator. Two of the necks serve for the entrance and exit of the air, and the third and vertical neck receives a corked tube, through which pieces of dried phosphorus are dropped at intervals into the dish.

Grabowski (*Annalen*, 1865, 136, 119) recommends for the preparation on the large scale the use of a sheet-iron cylinder, having a cover and resting on a sheet-iron funnel. The cover has a chimney closed by a cork, and a damper is fitted to the chimney so that the air may be admitted as required. The oxide produced is shaken at intervals into a bottle beneath the funnel.

This oxide is a white amorphous powder which, when pure, is perfectly colourless and odourless. It frequently possesses a garlic smell, from the presence of phosphorous oxide, and may have a yellowish colour, more noticeable when a portion is allowed to deliquesce, from presence of the lower oxide  $P_2O_3$  or of red phosphorus. To free the oxide from all traces of

lower oxides, it should be distilled over platinum sponge in a current of oxygen, until the product no longer reduces silver nitrate solution (Threlfall, Phil. Mag. 1893 [v.] 35, 14; Shemstone and Beck, Chem. Soc. Trans. 1893, 473). It rapidly deliquesces, with production of metaphosphoric acid. When added to water, phosphorous acid is gradually produced, with evolution of heat. According to Hautefeuille and Perrey (Compt. rend. 1884, 29, 33), it exists in three forms, crystalline, pulverulent and vitreous (Giran, *ibid.* 1903, 136, 550).

Phosphorus pentoxide is the best desiccating agent known, and is largely used in the laboratory for the desiccation of gases and liquids, and for the elements of water from compounds, as in the preparation of nitrogen pentoxide. Phosphorus pentoxide, when completely pure is capable of becoming highly reduced *in vacuo* (Ebert and Hoffmann, Z. anorg. Chem. 1900, 80).

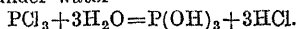
According to Besson (Compt. rend. 1897, 124, 763), the oxide  $P_2O_5$  also exists.

**Hypophosphorous acid**  $H_3PO_2$  is a monobasic acid the salts of which are formed when alkalis or alkaline earths are boiled with phosphorus. The barium salt  $Ba(PH_2O_2)_2$  is of most interest, as the acid and salts are usually prepared from it. This salt is formed, with evolution of hydrogen, on boiling phosphorus with water:  $-3Ba(OH)_2 + 2P_4 + 6H_2O \rightarrow 2Ba_3(PH_2O_2)_2 + 2PH_3$ . It may be decomposed by dilute sulphuric acid to obtain the acid, or by the addition of a sulphate to produce another hypophosphite (Marie, Compt. rend. 1904, 138, 1216).

Hypophosphorous acid forms a thick syrup, from which crystals melting at  $26.5^\circ$  (Marie) may be obtained by cooling below the boiling-point of the syrup, or cooling in a freezing mixture. When strongly heated, it decomposes into phosphoretted hydrogen and phosphoric acid. It reduces mercuric chloride to calomel or mercury (Sievert, Zeitsch. anorg. Chem. 1909, 64, 29), and is oxidised to phosphoric acid by chlorine and other oxidising agents (Steele, Chem. Soc. Proc. 1908, 193). When concentrated it attacks glass and porcelain more readily than phosphoric acid. Most hypophosphites dissolve in water, and many in alcohol. They are all powerful reducing agents, and precipitate gold and silver from solution. The sodium salt is used in medicine. For the preparation of hypophosphites, compare Kendal (J. Soc. Chem. Technol., 1908, 193).

According to Mai (Ber. 1902, 35, 162), hypophosphorous acid reacts with organic diazo compounds forming hydrocarbons, this being in some cases an advantageous method of forming the latter. When boiled with acetone, hypophosphorous acid yields crystalline products,  $H_3PO_2 \cdot 2C_3H_8O$ ;  $H_3PO_2 \cdot C_3H_8O$ ; and  $H_3PO_2 \cdot C_3H_8O$  (Marie, Compt. rend. 1901, 133, 219).

**Phosphorous acid**  $P(OH)_3$  is obtained by the action of water on phosphorous oxide or of moist air on phosphorus. The pure acid may be obtained by the action of phosphorus trichloride on water, or by the action of phosphorus trichloride on a deep layer of phosphorus melted under water—



On evaporating the solution until it attains a temperature of  $180^\circ$  and forms a thick syrup, it gives on cooling a crystalline mass melting at  $70.1^\circ$  (Thomson, Ber. 1874, 7, 996). When strongly heated, the acid produces phosphoretted hydrogen and phosphoric acid. The aqueous solution slowly absorbs oxygen. It is a powerful reducing agent, and precipitates gold, silver, and mercury from solution.

Phosphorous acid is tribasic, but, excepting the tribasic sodium salt and some ethereal salts, only two atoms of hydrogen are replaceable by the base. All phosphites are soluble in water, the normal alkaline salts being most soluble. They act as reducing agents similarly to the hypophosphites, but, unlike them, give a precipitate with lime water.

**Pyrophosphorous acid**  $H_4P_2O_5$  is obtained by passing the vapour of phosphorus trichloride volatilised by a stream of carbon dioxide through the product of the reaction of water on an excess of the trichloride for 20 hours. It is then placed in a vacuum over fused potash and phosphorus pentoxide. It can also be obtained by the continuous agitation for about 5 hours at  $30^\circ$ – $40^\circ$  of a mixture of phosphorous acid and phosphorus pentoxide. It melts at  $38^\circ$ , is soluble in water, and by water, at  $130^\circ$  gives off phosphine and at  $45^\circ$  in presence of phosphorus trichloride yields phosphorus and phosphoric or pyrophosphoric acid (Auger, Compt. rend. 1883, 136, 814). The pyrophosphites, such as  $Na_2P_2O_5$  also exist.

**Phosphoric acids.** Three acids, produced by the combination of phosphorus pentoxide with one, two, and three molecules of water respectively, are known, their names and composition being as follows: *Metaphosphoric acid*  $HPO_3$  or  $P_2O_5 \cdot H_2O$ ; *pyrophosphoric acid*  $H_4P_2O_5$  or  $P_2O_5 \cdot 2H_2O$ ; and *orthophosphoric acid*  $H_3PO_4$  or  $P_2O_5 \cdot 3H_2O$ . The sodium and silver salts of a fourth acid  $P_4O_{10}(HO)_6$  or  $2P_2O_5 \cdot 3H_2O$ , which may be called tetraphosphoric acid, are also known (Fleitmann and Henneberg, Annalen, 1848, 65, 324). Salzer (*ibid.* 1877, 187, 322) has described a phosphorus-phosphoric acid or hypophosphoric acid  $P_4O_{10}(HO)_8$  of which phosphorus tetroxide may perhaps be the anhydride (Rosenheim and Pritze, Ber. 1908, 41, 2708). Finally, the sodium salt of *thiophosphoric acid*  $H_3PSO_3$  (Wurtz, Ann. Chim. Phys. [iii.] 20, 472), and the salts of di- and tri- thiophosphoric acid,  $H_2PS_2O_2$  and  $H_2PS_3O_5$  are also known (Kubierschky, J. pr. Chem. 1885, [ii.] 31, 93).

Several series of thiophosphates have been prepared by heating the metals with phosphorus and sulphur (Ferrand, Bull. Soc. chim. 1895, [iii.] 13, 115; Compt. rend. 1896, 122, 886).

**Orthophosphoric acid**  $H_3PO_4$ , usually known as 'phosphoric acid,' is a tribasic acid which is produced when amorphous phosphorus is heated with concentrated nitric acid (Watson, J. Soc. Chem. Ind. 1892, 224). The phosphorus slowly dissolves, with evolution of red fumes, and the solution is evaporated in a dish with repeated additions of nitric acid until red fumes cease to be evolved, to ensure the absence of phosphorous acid.

The acid is prepared commercially from bone-ash by digesting 3 parts of the ash with 3 parts of crude sulphuric acid (1.55) and 18 or 20 parts of water for two or three days. The

solution, which contains the phosphorus as calcium tetrahydric diphosphate ('superphosphate of lime'), is then pressed in linen filters from the precipitated calcium sulphate, and is concentrated to a syrup, treated with concentrated sulphuric acid to precipitate the lime, and the solution filtered off, evaporated, and heated to remove the sulphuric acid. By another process the solution is treated with ammonium carbonate, which precipitates the lime and leaves triammonium phosphate in solution. The solution is separated and evaporated, and ignited to expel the ammonia. The acid obtained by either method contains magnesia and other impurities.

In another process, phosphorus is dissolved in its own pentoxide, the acid of sp.gr. 1.18, diluted with 4 parts of water and  $1\frac{1}{2}$  parts of sodium sulphate is added. The filtered solution is neutralised while hot with sodium carbonate, refiltered, and precipitated with barium chloride. The mixture of barium sulphate and phosphate thus obtained is decomposed by sulphuric acid.

The bones, apatite or horn piths, &c., may be dried, ground, and digested with aqueous phosphoric acid, after which the product is treated with sulphuric acid (Lomas, J. Soc. Chem. Ind. 1900, 836; Eng. Pat. 9611).

According to Maywald (J. Soc. Chem. Ind. 1908, 1161), phosphoric acid may be manufactured by maintaining a low potential arc produced by a current of 60 volts, in a granular mass of phosphorus to which air has access: the phosphoric acid is condensed and collected. By this method, phosphoric acids are described by Maywald, J. Soc. Chem. Ind. 1902, 1533; Powter, *ibid.* 1904, 252; Bandon, *ibid.* 1904, 787).

Commercial phosphoric acid frequently contains arsenic, either from the phosphorus used or from the acid employed in dissolving the bones, &c. The arsenic may be removed by reducing it to arsenious oxide with sulphuric acid, and precipitating it by passage through hydrogen, after removing the excess of the sulphurous acid by boiling.

To avoid the necessity for removing the arsenic, Wenzell (Proc. Am. Pharm. Assoc. 1882, 556, and Pharm. J. [iii.] 14, 24) prepared the acid by the slow, spontaneous oxidation of phosphorus in trays containing a thin layer of water. The phosphorous acid thus produced contains the arsenic as arsenious oxide, which becomes reduced to the elemental state, so that it may be separated by filtration, when the solution is heated to about 190° for half an hour. The filtered solution is oxidised to phosphoric acid by the action of nitric acid (Baker, J. Soc. Chem. Ind. 1885, 574).

To prepare the pure acid the commercial acid may be precipitated as the lead salt by addition of lead acetate, the precipitate being washed and decomposed by passage through hydrogen, or by treating it with dilute sulphuric acid. In the latter case the solution must be heated to remove sulphuric acid, and freed from traces of lead by means of hydrogen.

Phosphoric acid is used for various purposes is

also prepared by dissolving the pentoxide in water.

According to Nicolas (Compt. rend. 1890, 111, 974), pure phosphoric acid may be prepared by gradually adding pure calcium phosphate to a slight excess of pure dilute hydrofluoric acid contained in a lead or platinum vessel, the mixture being well stirred after each addition. The high temperature of the mixture is maintained for some time to complete the reaction; the calcium fluoride formed is removed by filtration and the filtrate, consisting of a solution of phosphoric acid, is evaporated until a thick syrup is obtained. By further evaporation, meta- and pyrophosphoric acids can be obtained.

By evaporation of its solution *in vacuo* over sulphuric acid, orthophosphoric acid may be obtained in hard, transparent, deliquescent, six-sided ortho-rhombic prisms fusing at 38.6° and losing water at 160°. At about 215° the acid is converted into metaphosphoric acid, and when heated until the acid begins to evolve, the evolved is converted into a highly deliquescent glassy mass of metaphosphoric acid.

The strength of aqueous solutions at 15.5° is shown in the following table (J. Watts, Chem. News, 1865, 12, 160):—

Specific gravity	P <sub>2</sub> O <sub>5</sub> in 100 parts	Specific gravity	P <sub>2</sub> O <sub>5</sub> in 100 parts
1.508	49.60	1.247	28.24
1.492	48.41	1.236	27.30
1.476	47.10	1.226	26.30
1.464	45.63	1.211	24.79
1.453	45.38	1.197	23.23
1.442	44.13	1.185	22.07
1.434	43.95	1.173	20.91
1.426	43.28	1.162	19.73
1.418	42.61	1.153	18.81
1.401	41.60	1.144	17.89
1.392	40.86	1.136	16.95
1.384	40.12	1.124	15.64
1.376	39.66	1.113	14.33
1.369	39.21	1.109	13.25
1.356	38.00	1.095	12.18
1.349	37.37	1.081	10.44
1.339	36.74	1.073	9.53
1.328	36.15	1.066	8.62
1.315	34.82	1.056	7.39
1.302	33.49	1.047	6.17
1.293	32.71	1.031	4.15
1.285	31.94	1.022	3.03
1.276	31.03	1.014	1.91
1.268	30.13	1.006	0.79
1.257	29.16		

A simple method of determining the strength of phosphoric acid, as used in pharmacy, is to transfer the solution to be tested into a graduated flask and to add an excess of N/1 ammonia solution followed by an excess of a saturated neutral solution of magnesium sulphate. The liquid is then diluted to the mark on the flask, well shaken and filtered, and the residual ammonia is then titrated in an aliquot part of the filtrate (Segalle, Zeitsch. anal. Chem. 1895, 33).

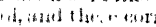
Phosphoric acid attacks glass, porcelain, and

other alkali, and fused them at a temperature above 300°, alkyl phosphate and phosphates of the base being formed. It dissolves ferrosilicic acid, ferrosilicon and spiegeleisen, but the silicic acid of the latter remains undissolved (Hyron, *J. Soc. Chem. Ind.*, 1902, 214).

When present in sufficient quantity, phosphoric acid increases the translucency and improves the colour of pottery bodies. It also acts as a flux and vitrifying agent (Parmelee, *Trans. Amer. Ceramic Soc.*, 1906, 8, 236).

Both ortho- and pyro-phosphoric acids form a series of hydrates, those of the latter being soluble and readily passing into the ortho condition (Giran, *Compt. rend.*, 146, 1279; Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, 31, 1189).

The pyro-acid possesses three degrees of acidity, the first that of a strong acid, the second that of a weak and like acetic, the third that of an alcohol, and these correspond with the formation of mono-, di- and tri-basic phosphates (Berthelot, *Compt. rend.*, 132, 1277, 1517; Cavalier, *ibid.*, 1399), of which the sodium salts may be taken as types. They include the normal or sodium phosphate  $\text{Na}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , the hydrogen sodium phosphate  $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , and the di-hydrogen sodium phosphate



The normal alkaline salts are readily soluble and possess an alkaline reaction. The insoluble neutral phosphates are converted by dilute acid, even by carbon dioxide, into the soluble hydrogen phosphates. Hydrogen di-sodium phosphates and corresponding salts are obtained by changing a solution of the hydroxide or carbonate of the base to phosphoric acid until weakly alkaline. The hydrogen phosphates of the alkalis are soluble and lightly acid. When strongly heated they produce metaphosphates with evolution of water.

The phosphates, which can be freed from phosphoric acid by heating them in a current of chlorine and carbon tetrachloride (Jannasch and Dufur, *J. pr. Chem.*, 1908, [n.] 78, 21), are, according to Speck and Hunschel, *Zeitsch. Farben und Textil. Ind.*, 1905, 4, 297, very effective in removing dyeing processes. This is particularly true of the alkali salts.

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When heated phosphoric acid is heated with phosphoric acid, the product, after neutralising with barium carbonate and filtering, is decomposed with the calculated amount of sulphuric acid, glycerophosphoric acid is obtained (Bate and Fraser, *J. Pharm. Chim.*, 1901, 333; Aron and Tillaud, *ibid.*, 1898, [v.] 1, 229; *Compt. rend.*, 1898, 126, 1215; *Bull. Soc. Chim.*, 1898, 15, 684; Tubert and Belugon, *ibid.*, 21, 363; Carré, *Compt. rend.*, 1901, 133, 183; 1903, 137, 1070; 1904, 138, 47). Glycerophosphoric acid yields normal and acid salts with the metal, and also combines with organic bases such as quinine, cocaine, &c. Phosphoric acid also reacts with mannitol (Carré, *ibid.*, 1903, 136, 306).

Phosphoric acid esters can be prepared by heating together a halogen or fatty acid derivative and a sugar (2 mol.) with phosphoric acid (1 mol.) and water (1 mol.) (Ulzer and Reiss, *J. Soc. Chem. Ind.*, 1908, 713; D. R. P. 191489; Arbuzoff, *Ber.*, 1905, 38,

1171; Carré, *Ann. Chim. Phys.*, 1905, [viii.] 5, 345; Young, *Chem. Soc. Proc.*, 1907, 65).

**Pyrophosphoric acid**  $\text{H}_4\text{P}_2\text{O}_7$  is obtained by heating orthophosphoric acid to 215° for some time (Giran, *Compt. rend.*, 1902, 134, 1499; 1902, 135, 961; Rosenheim and Pritze, *l.c.*). It occurs either as a soft glass or as an opaque crystalline mass; crystals separate from the syrupy acid at -16° and melt at 61° (Giran, *l.c.*). It may be obtained in solution by precipitating the sodium salt with lead acetate and decomposing the precipitate with sulphuretted hydrogen. When heated in solution it is converted into orthophosphoric acid (Berthelot and André, *Compt. rend.*, 1896, 123, 776; Montemartini and Egidi, *Gazz. chim. ital.*, 1902, 32, i, 381).

Pyrophosphates are obtained by heating the mono-hydrogen phosphates, or by addition of the base to the acid. Both normal and acid sodium and other alkaline pyrophosphates, having an alkaline and an acid reaction respectively, are known. When heated with an acid they are converted into orthophosphates (Ridenour, *Chem. Zentr.*, 1900, 1, 834).

**Metaphosphoric acid**  $\text{HPO}_3$  is obtained as a deliquescent glassy mass. When the acid is heated until dense fumes of  $\text{P}_2\text{O}_5$  be evolved. It is then known as *glacial phosphoric acid*, and usually contains sodium phosphate, which communicates hardness to the otherwise soft acid (Brescius, *Zeitsch. anal. Chem.*, 6, 187; Betten-dorf, *ibid.*, 27, 24).

It is also obtained by the spontaneous deliquescence of phosphorus pentoxide.

On standing at the ordinary temperature, or more rapidly when boiled, metaphosphoric acid is changed into the ordinary ortho-acid (Berthelot and André, *Compt. rend.*, 1897, 124, 265; Montemartini and Egidi, *Gazz. chim. ital.*, 1901, i, 31, 394).

Metaphosphoric acid volatilises at a bright-red heat. Its salts are prepared by neutralising the acid or by heating a dihydric orthophosphate. Among the salts no less than five modifications are known. They may be regarded as salts of polymeric metaphosphoric acids, and are respectively known as mono-, di-, tri-, tetra-, and hexameta-phosphates.

Various esters, alkyl and other organic derivatives of phosphorus have been prepared (Giran, *Compt. rend.*, 1898, 126, 592; Cavalier, *ibid.*, 1898, 127, 60; 1906, 142, 885; Pfeiffer, *Ber.*, 1904, 37, 4620; Rosenheim and Levy, *Zeitsch. anorg. Chem.*, 1905, 43, 34; Hibbert, *Ber.*, 1905, 38, 160; Lamont, *Compt. rend.*, 1905, 141, 1241; Berthaud, *ibid.*, 1906, 143, 1116; Barber, *Monatsh.*, 1906, 27, 379; Anschütz, *Annalen*, 1907, 358, 92; Michaelis and Linke, *Ber.*, 1907, 40, 3419; Autenrieth and Geyer, *ibid.*, 1908, 41, 146; Pistchmuka, *ibid.*, 385, 4; Atti. R. Acad. Lincei, 1908, [v.] 17, i, 847; Swartz, *Bull. Acad. Roy. Belg.*, 1909, 60; Luff and Kipping, *Chem. Soc. Trans.*, 1909, 1993; Arbuzoff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 395).

For detection and estimation of phosphoric acid *v. ANALYSIS*.

**PHOTOGRAPHY. Historical. Introduction.**—Photography is the art by means of which

images of various objects may be formed by specially constructed lenses on sensitive films, and there rendered visible and permanent by certain chemical processes.

The effect of light in changing the nature of chemical substances, more especially certain salts of silver, was known to the ancients, but no use was made of such changes until the experiments of Scheele first demonstrated the action of the solar rays on these salts. Count Rumford and Ritter showed that these actions were produced chiefly by invisible rays; but no practical use was made of the discovery of this action of light until Thomas Wedgwood in 1802 published his method of producing sun-pictures on white paper impregnated with a salt of silver.

Daguerre and Niepce, taking advantage of the camera obscura invented by Baptista Porta, succeeded in rendering the images produced by its lenses permanent; and from a long series of experiments devised the process of the Daguerrotype. To Niepce is due the credit of being the first to notice the fact, that the action of light was capable of rendering bitumen insoluble in its ordinary solvents, and that by placing a drawing which had been varnished to make it transparent over a plate covered with a thin layer of bitumen, and exposing the whole to the sun, the parts uncovered by the lines of the drawing could be dissolved away by certain solvents. These early experiments laid the foundation of the modern method of producing copies known under the name of Heliography or Collotype.

A period now followed in which many experiments conducted by Wedgwood, Herschel, and others were carried out on silver compounds; but they proved unsuccessful, chiefly owing to the inability to render the copies made with the silver salts fixed or permanent. Some years afterwards Herschel showed that sodium thio-sulphate might be used as a fixing agent, and this substance is employed at the present day. Niepce and Daguerre made experiments on silver iodide as the sensitive material. Their experiments resulting in the establishment of the Daguerrotype. In this process a silver plate is treated with iodine, and then exposed in the camera. After exposure it is placed in a properly-constructed box and the image developed by the vapour of mercury. Daguerre was thus able to produce a moderately-sensitive film, and many of the portraits done by the Daguerrotype process still exist in a remarkably good condition.

About the same time Fox Talbot introduced the process known as the Talbotype, in which waxed and iodised paper treated with a silver salt was employed. This paper was more sensitive than the materials previously employed, whereby the exposure necessary was much shortened, the image being developed with gallic acid. These pictures were termed 'negatives' by Talbot, as the lights and shadows were reversed; to produce a 'positive' from these a second sheet of sensitive paper was exposed under the 'negative.' The work of Talbot forms the basis of the more modern processes, and the names of 'positive' and 'negative' introduced by him are still retained.

These inventions were overshadowed by the introduction of the 'wet collodion pro-

cess' by Scott Archer in 1851, whereby the exposure necessary was reduced to a still shorter time. This process differed from the Talbotype in employing glass as a substratum for the sensitive material, and this, coated with collodion containing the soluble halogen salts, formed the sensitive silver compound by double decomposition on the film. The sensitive plate, being transferred to the camera, was exposed to the light, and the invisible image produced was developed in the dark room in a manner afterwards to be described.

For a long time the wet collodion process held its own; but gradually the advantages to be obtained from a plate sensitised so as to keep without deterioration for some length of time began to be felt, and plates prepared either with a collodion or gelatin emulsion have supplanted, except for certain purposes, the wet plate process. At first dry plates consisted of those prepared in the silver bath, which, after being sensitised and washed, were dipped in some preservative material capable of retaining the sensitiveness of the film for considerable periods. These rapidly gave place to the process now in use, where the sensitive salts, mixed with warm solutions of gelatin, are spread upon glass plates. When dry the plates are ready for use and will apparently keep in a perfect condition for a long period of time. These modern plates differ from the older form of wet plate in being enormously more sensitive, and have thus rendered possible the photography of moving objects and subjects on.

In 1871, R. L. Maddox produced some successful photographs with gelatin emulsion, and a little later they were commercially prepared and introduced for sale by R. Kennett and Burgess. A still more sensitive emulsion was devised by Bennett about 1878, which was produced by prolonged digestion of the prepared mixture at 32°, and finally the discovery that the finished emulsion could be rendered still more rapid by the addition of ammonia in its formation, has given us the numerous and rapid plates which are now to be procured.

In later years the principal improvements in the manufacture of photographic plates have been altered. The improvements introduced in manufacture and development have largely been in the direction of introducing into the films substances which render them more sensitive to rays of light other than the violet, and thus rendering possible the more modern processes for isochromatic and panchromatic photography.

*Apparatus.*—The apparatus employed in photographic work, special textbooks must be consulted. There are, however, two important pieces—the lens, and the camera—about which a short description may be given.

The lenses in general use for photographic purposes are: (a) simple lenses; (b) unsymmetrical doublets; (c) symmetrical doublets; (d) triple combinations; (e) anastigmatic combinations; (f) telephoto objectives; (g) achromatic combinations. Although the first have been termed 'single lenses,' it must be understood that photographic lenses are

combinations of two or more simple lenses, and the term 'single lens' here refers to the fact that only one combination is used, instead of two or more, as in the other or more perfect lenses.

The single lens (Fig. 1) consists generally of a combination of two or more lenses, arranged as a combination in the tube of the lens at the end nearest the camera; the convex side of the combination being towards the plate. This is a good lens with which to begin photographic work. It is fairly rapid with a moderately wide angle, and gives good definition. It is not, however, applicable to the photography of large

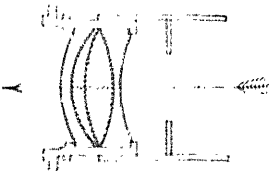


FIG. 1.—SINGLE CONVERTIBLE LANDSCAPE LENS.

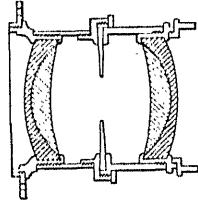


FIG. 2.—RAPID RECTILINEAR LENS.

buildings near at hand, as the marginal rays suffer distortion.

A rectilinear or symmetrical lens (Fig. 2) consists of two combinations, arranged at the ends of the brass tube, front and back. These combinations are the same in both directions of vision, converging meniscus lens occupying the inside positions in the tube. This is a useful lens, giving practically no distortion and possessing a fairly wide angle.

A symmetrical wide angle lens is constructed much in the same way, and has two combinations formed of meniscus lenses but of much deeper curvature than those employed in other combinations, and placed closer together in the lens tube. Such lenses take in a very wide angle and are specially suited for photographing buildings and portions of landscape in cramped situations. They are somewhat slower than other combinations, but give no appreciable distortion.

The lens for portraiture (Fig. 3) is constructed to get the greatest amount of rapidity, but although possessing that advantage it has some defects. It consists of a back and front combination arranged at some little distance apart. The front combination contains a double convex and a plane-concave lens cemented together, the double convex lens taking the position next the object; the back combination consists of a double convex and a diverging meniscus lens, which are frequently mounted so as to leave a small space between the two lenses. The double convex lens is placed in the tube in the position next the camera.

With the dry plates now obtainable great rapidity can be got with this lens, but it has little depth of focus, poor marginal definition, and presents a rounded field. It is devised for portraiture, and is well adapted to that purpose. In some of the newer lenses constructed on this principle great improvements have been made,

diminishing these disadvantages and rendering the lenses useful as universal lenses.

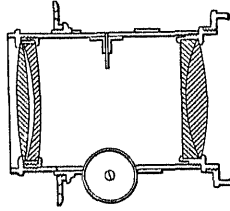


FIG. 3.—PORTRAIT COMBINATION.

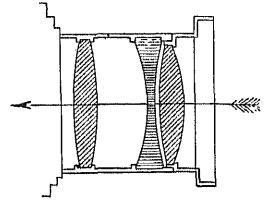


FIG. 4.—COOKE LENS.

Fig. 4 represents the arrangement of the lenses in what is known as the Cooke lens which is much used for hand cameras and in general landscape work. With a wide aperture it covers plates corresponding to the size of the lens well up to the margin, and when stopped down will cover larger plates like a wide angle lens. These lenses are free from distortion and free from spherical and chromatic aberration.

Fig. 5 represents the arrangement in the telephoto lens suitable for obtaining views of inaccessible objects.

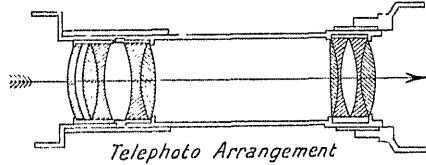


FIG. 5.

*The Camera.* This consists of a box, made of wood, or, preferably, as in the modern cameras, a framework of wood with a bellows-expanding body of leather, so that when closed the camera may occupy little space and be comparatively light. In front of the camera is placed the lens, and at the back a plate of ground glass, on which the image of the object to be photographed may be focussed, together with an arrangement for lengthening or shortening the body of the camera. The position of the ground-glass screen is the same as that occupied subsequently by the sensitive plate.

Accompanying the camera are one or more double-backed dark slides, arranged to carry two dry plates each, back to back, with a blackened slip of thin sheet iron between them and a sliding shutter, so as to expose the plate when in the camera. In the case of wet-plate work, it is customary to use a dark slide holding only one plate. The dark slides of larger cameras may be fitted with light wooden carriers, which allow of smaller plates being used. For the exposure in the camera of flexible material coated with emulsion other arrangements, such as roller slides, are required, on which the material may be stretched. A description of these will be found under the section describing paper negatives and stripping films. The camera should be made of light and well-seasoned wood, and the body of good leather. It should be capable of opening out to a length two or three times as much as the



length of the largest plate it carries. The corners may be brass-bound, especially for cameras required in hot climates. The front, carrying the lens, should be provided with a vertical and a horizontal adjustment, so that the position of the lens in these directions may be changed at will without altering the position of the camera. The back of the instrument should have a certain degree of swing, so that the angle between the sensitive plate and the axis of the lens may be varied when required. By such freedom of movement it is possible to obtain considerable improvement in the adjustment of the forms of objects at different distances and in peculiar positions.

To obviate the necessity of dark backs, cameras have been designed in which a separate slide for the plates is dispensed with, and its place taken by a multiplex back, containing about eight or more plates, which, by a mechanical arrangement, can be alternately exposed to the light. Other more modern cameras have from time to time been introduced where continuous films on rollers may be used.

The support for the camera should be as strong and steady as possible consistent with lightness. For out-door work the camera stand is generally made to fold up, so as to make it more portable, and in most cases the legs of the stand have a sliding adjustment, which is a matter of importance when working on unequal ground. The most important requirement of a stand is perfect rigidity when fixed, so that no vibration may be communicated to the camera during exposure.

*Action of light on silver compounds.* Although many chemical substances undergo change by light, the halogen compounds of silver are those generally employed in photography, and they may be taken to illustrate such changes, as well as those taking place in the further processes of development and intensification.

Of the composition of the latent image we have no exact knowledge. It is generally accepted, however, that the change, so far as the halogen silver salts are concerned, is the conversion of these into sub-salts, as may be shown by silver bromide,  $2\text{AgBr} = \text{Ag}_2\text{Br} + \text{Br}$ , this change being common to the three halogen salts. Experiments have, however, shown that the change may be probably of a much more complicated kind. Whatever its exact nature may be, there is evidence to show that it will not take place with any facility unless some agent is present which will absorb the halogen as it is liberated during the change. Such agents are to be found in certain metallic salts and in organic substances. In the wet collodion process the presence of excess of silver nitrate on the surface of the sensitive plate acts as such an absorbent. To trace the extent to which such silver compounds, either alone or when mixed, are sensitive to the action of light, the examination must be made by photographing the solar spectrum. This has been extensively done by Abney, Vogel, and many others, and the conclusions may be drawn from

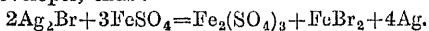
The action of the light is different for each of the halogen salts of silver, either alone or when mixed.

It differs also according to the material with which the sensitive compound may be mixed or on which it may be spread, whether at the time of exposure to light the material be in a moist or in a dry condition, and, finally, the different quantities in which the sensitive compounds may be mixed together.

*Chemical action in development of the image.* As the action of light would have to be immensely prolonged to produce a visible image on the sensitive film, reagents are employed which, exercising a reducing action on the silver salts, render visible the action begun by the light. Such agents are termed developers.

The action which takes place in the development of wet collodion plates, may be illustrated by the action of ferrous sulphate on silver nitrate,

$6\text{AgNO}_3 + 6\text{FeSO}_4 = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{NO}_3)_6 + 3\text{Ag}_2$ ,  
in which it is assumed that the silver so deposited adds itself to the silver salt already changed by the action of the light, and decomposed by the developer, thus:



The developed image in the wet plate is essentially on the surface of the film, because the silver salt is on top of the film. If the ferrous salt and silver nitrate be brought together alone, too rapid reduction takes place. It is customary, therefore, to employ certain substances which act as restrainers during the decomposition. These are to be found in either mineral or organic acids, and in certain other organic compounds.

Development may also be carried out with organic salts of iron, of which the most important is ferrous oxalate:

$2\text{Ag}_2\text{Br} + 3(\text{FeC}_2\text{O}_4) = \text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{FeBr}_2 + 4\text{Ag}$ ,  
a change comparable with that of the ferrous sulphate just described.

Besides iron oxalate, pyrogallol is employed, both in the wet and in the dry-plate processes, the action here, as in the case of iron salts, being one of reduction in the presence of some halogen absorbent. In alkaline development the reducing or developing action takes place first on silver sub-bromide, produced by the action of light on the bromide, the bromine thus set free, being absorbed by the organic substratum. In this development the change is produced by pyrogallol rendered alkaline by ammonia or some other alkaline substance, the pyrogallol alone being unable to effect the reduction of the sub-bromide to metallic silver. In the presence of an alkali, however, it becomes a rapid absorbent of oxygen, or of an equivalent of chlorine, bromine or iodine.

As there seems reason to believe that freshly-deposited silver converts unaltered silver bromide into the sub-bromide, and as this sub-bromide, on being attacked by the developer, would at once give a deposit extending over the plate farther than the area of the action of the light, it is necessary to have with the developer some substance capable of acting as a restrainer on the secondary decomposition. Generally, soluble bromides are employed for this purpose, and it is possible that they form a double salt with the nascent silver, so obviating a deposit except where the light has begun the action.

It must be understood that our present knowledge of the action of light and of developers on silver salts is not sufficient to enable equations to be written which exactly the changes which occur.

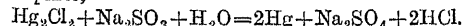
The idea of ionisation has been introduced to explain the chemistry of development. Thus in the case of *hydroquinone*, where it is known that the *quinone* is formed during development is *quinone*, the *hydroquinone* is supposed to become ionised, thus losing during the action two negative charges which neutralise the positive charges of the silver in the ionised silver bromide, the oxygen atoms combining to form *quinone*.

*Chemical actions in intensification, reduction, and fixation of negatives.* In the process of intensification we have a strengthening of the developed image, which may be brought about in two ways: either by causing a further deposition of silver, or a deposition of some other substance on the silver already deposited during development.

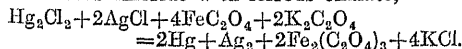
In the first case the change is analogous to that of development. As an instance of the second the following may be taken:

$\text{Ag}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} = 2\text{AgCl} + \text{H}_2\text{O}$   
 $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} = \text{NH}_4\text{Hg}_2\text{Cl}_2 + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$   
 when in the first place the silver deposited on the plate, on treatment with mercuric chloride, yields mercurous and silver chlorides. On application of ammonia solution to this, after washing, we have the image darkened by the formation of black dimercurous-ammonium chloride.

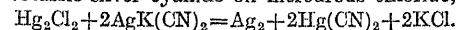
Other intensifying agents are employed, of which the following are the most important:—Mercurous chloride, after washing with sodium sulphite,



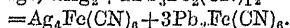
Mercurous chloride with ferrous oxalate,



Potassio-silver cyanide on mercurous chloride,

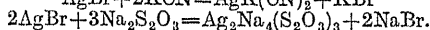


The ferrocyanides of lead or uranium on the silver image,  $2\text{Ag}_2 + 2\text{Pb}_3\text{Fe}_2(\text{CN})_{12}$



The substances formed in this case, being white, are, after washing, treated with an alkaline sulphide to convert them into the dark sulphides. The ferrocyanide of uranium, possessing a dark brown colour, renders the picture sufficiently dense without further treatment.

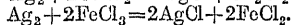
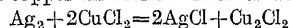
*Fixing the negative.* This is generally done with sodium *thiosulphate* or potassium cyanide, the action of which depends upon the formation of soluble double salts of silver with the alkali metals, which can be washed away from the negative. In fixing by sodium *thiosulphate*, it is necessary that the solution should be concentrated, otherwise an insoluble double salt may be produced. The action in each case may be represented by the following equations:



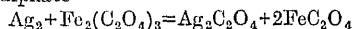
*Reducing negatives.* It often happens that a negative becomes too dense during the process of development, and it is necessary to reduce its density. This may be done either by mechanical

or chemical means. In the application of chemical means two actions may take place, (1) the image may be converted into one of another or less dense colour, or (2) the excess of silver deposit may be removed; the latter is the best course, and is done by transforming the silver into silver chloride or bromide, and removing that by solution. Many substances effect this change, such as cupric and ferric chlorides, bleaching powder solutions, sodium and potassium *hypochlorite*, ammonium and potassium *perchlorate*. Silver reduces these salts, becoming itself converted into chloride, which may be removed by again fixing.

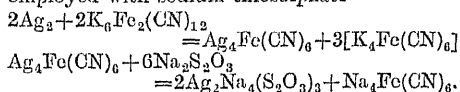
With copper and ferric chlorides we have



These methods have the disadvantage of not showing the full diminution in density till the whole of the  $\text{AgCl}$  has been removed by the fixing agent. To allow of the final reducing action being seen during the operation, a process has been introduced by which *potassio-ferric oxalate* is simultaneously used with sodium *thiosulphate*



$\text{Ag}_2\text{C}_2\text{O}_4 + 3\text{Na}_2\text{S}_2\text{O}_3 = \text{Ag}_2\text{Na}_4(\text{S}_2\text{O}_3)_3 + \text{Na}_2\text{C}_2\text{O}_4$   
 (Eder). Potassium ferrocyanide may also be employed with sodium *thiosulphate*



*Preparing and edging plates.* To prepare glass plates for coating—either with collodion in the wet-plate process, or for the more modern processes with emulsions—it is necessary, if they have been used before, that all the old film should be removed; and whether they have been used or not, to polish them so as to receive the fresh coating. Old varnished films may be removed by soaking the plates for 24 hours in solutions of hydrochloric or nitric acid containing 1 part of the acid to 20 parts of water. After this time the film can be easily removed by brushing with a nail brush and warm water. After removal of the film the plate should then receive a polish, so that the coating may flow easily over the surface. This is best done with ordinary whiting and water made up to a creamy consistency, or, what has proved very effectual in the writer's experience, rouge made up to the same consistency with alcohol, and a few drops of ammonia added to it to dissolve grease stains. The plate is laid on a pad of thick flannel, a little of the fluid containing the rouge is poured on the plate, which is gently rubbed with a small pad of flannel. The alcohol gradually evaporating leaves the plate covered with a thin film of dry rouge, which is best removed by gently polishing with a pad of tissue paper, the final polish to the plate being given with a second pad. If whiting and water are used, the powder, when dry, must be removed with a slightly-damped cloth, and however perfect the cloth may be, it is apt to leave shreds on the surface of the plate, which may be obviated by using the tissue paper.

When cleaned, it is customary to give the plate an edging or substratum of some material which will assist the collodion or the emulsion

to stick more firmly to the plate during the subsequent processes of washing, &c. In dry plates it is not always absolutely necessary to employ an edging, but is sometimes advisable, and is almost imperative with collodion films. The following solutions will be found sufficient for substrata:—

—	a	b	c	d	e
Albumen	White of 1 egg	Dried 50 grs.	—	—	—
Gelatin	—	—	75 grs.	—	—
Ammonia	5 mm.	5 mm.	2 drs.	—	—
India-rubber	—	—	—	5 grs.	5 grs.
Chloroform	—	—	—	5 oz.	—
Benzene (rectified)	—	—	—	—	5 oz.
Water	60 oz.	50 oz.	60 oz.	—	—

*a* and *b* must be filtered before use through a light plug of cotton-wool. In *a*, *b*, and *c* the plates may be immersed entirely in the solution, and placed on the rack to dry. In *d* and *e* the solution should be poured on as described for coating with collodion, or an edging of about a quarter of an inch may be given with a brush.

#### THE COLLODION PROCESS.

Although gelatin emulsion plates are now extensively used for ordinary photography, collodion plates are still employed in process work, and any account of the subject would be incomplete without a description of this process which for long was the only one in use.

The process depends upon the coating of glass plates with a stratum of soluble pyroxyline or collodion, impregnated with soluble iodides or bromides, which form the sensitive silver compound when placed in a solution of silver nitrate.

The *soluble pyroxyline or collodion cotton*  $C_{12}H_{21}O_6(OH)(NO_3)_2$  is formed by the action of a mixture of nitric and sulphuric acids with a little water ( $HNO_3$  with  $H_2SO_4$  and  $1\frac{1}{2}H_2O$ ), or of a mixture of potassium nitrate with sulphuric acid upon cotton. It differs from cotton in being soluble in a mixture of alcohol and ether, yielding a viscous fluid, which on evaporation leaves the pellicle or film of collodion.

To prepare the soluble cotton for collodion, 3 measured ounces of nitric acid (sp.gr. 1.457) are mixed with 2 ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp.gr. 1.845) are then added to this mixture with constant stirring, and the mixture allowed to cool to 60°. 100 grains of dry cotton, in tufts of about 10 grains each, are immersed in the mixture of acids and allowed to remain from 5 to 10 minutes in a covered beaker. The acid is then poured off, the cotton squeezed with a glass-rod, washed in a stream of water until all acid has disappeared, and finally dried by exposure to the air. Before drying, the cotton may be washed with a little weak solution of sodium carbonate to ensure the total removal of the acid.

The cotton employed must be entirely cleansed of all resinous matter adhering to it. For this purpose it should be boiled in sodium carbonate, thoroughly washed, and finally dried before immersion in the mixed acids.

For larger quantities of pyroxyline the following amounts of the different acids may be taken:

Sulphuric acid, sp.gr. 1.845	18 oz. fl.
Nitric acid, sp.gr. 1.457	6 "
Water	5-5½ "

The nitric acid is first added to the water, and lastly the sulphuric acid, the mixture being stirred and allowed to cool. These quantities of acid will convert about 300 grains of cotton.

For the manufacture of pyroxyline by the second method with potassium nitrate, the following quantities will be found useful:

Sulphuric acid	6 oz. fl.
Dried potassium nitrate	3½ oz. (av.)
Water	1 oz. fl.

The acid and water are first mixed together, and the dried potassium nitrate then added gradually in a finely-crushed condition. On stirring, a transparent viscous liquid is obtained, which must be kept at a temperature of 52°. Into this about 60 grains of dried cotton are then dipped in the manner previously described, and allowed to remain in the mixture for 10 minutes.

To form *collodion* the pyroxyline is dissolved in a mixture of alcohol and ether with the necessary quantities of soluble iodides and bromides to form the sensitive salt when the plate is immersed in the silver bath. The following quantities will give good general results:—

—	i.	ii.	iii.
Pyroxyline	120 grs.	120 grs.	100 grs.
Ether, sp.gr. 0.725	10 oz.	10 oz.	10 oz.
Alcohol, sp.gr. 0.805	4 oz.	5 oz.	5 oz.
Ammonium iodide	30 grs.	40 grs.	50 grs.
Cadmium iodide	45 grs.	40 grs.	—
Cadmium bromide	—	20 grs.	—
Alcohol, sp.gr. 0.830	4 oz.	5 oz.	5 oz.
Ammonium bromide	—	—	25 grs.

The pyroxyline is first dissolved in the mixed alcohol and ether; the iodides and bromides are then dissolved in the weaker alcohol and the two solutions mixed. i. gives a simple iodised collodion, ii. a bromo-iodised collodion, both suitable for negatives; iii. a collodion suitable for positives or ferrotypes.

The *sensitising bath*. The silver salt employed in the manufacture of this bath is silver nitrate, and the strength for the ordinary bath is from 35 to 40 grains of silver nitrate to the ounce of water except in certain cases. About 1½ grain of potassium iodide should be added for every 40 grains of silver nitrate; or the bath may be allowed to become saturated with silver iodide during the subsequent working.

To make the bath, from a quarter to half the quantity of water to be employed is taken, and in it the silver nitrate is dissolved; to this solution is added the soluble iodide, causing a precipitate of silver iodide gradually dissolving on shaking; the remainder of the water is then added, the mixture allowed to stand, and filtered. After preparation the bath should be slightly acid, and for this a drop or two of nitric or acetic acid may be added, preferably the

former. Should the bath be too acid after making, a little sodium carbonate may be added. The following are convenient quantities for the preparation of larger amounts of bath solution—

	For negatives	For positives
Silver nitrate (recrystallised)	6 oz.	5 oz.
Distilled water	80 oz.	80 oz.
Nitric acid	10 min.	12 min.

Saturate with an iodide as before described, and filter.

*Development of the latent image.* The chemistry of the action of the wet plate process has been already indicated. It is only necessary now to give formulæ best adapted to the development of the image. Those relate particularly to the acid development collodion process.

The following table gives the quantities necessary for some useful iron developers for wet plates:—

—	a	b	c	d
Ferrous sulphate	75 grs.	180 grs.	100 grs.	—
Ammonio-ferrous sulphate	—	—	—	125 grs.
Copper sulphate	—	—	50 grs.	—
Barium nitrate <sup>1</sup>	—	120 grs.	—	—
Acetic acid	120 min.	120 min.	100 min.	125 min.
Alcohol	120 „	—	100 „	125 „
Nitric acid	3 „	10 min.	—	—
Water	5 oz.	5 oz.	5 oz.	5 oz.

In the wet-plate process the development may be carried out in sufficient quantity of the fluid, or the plate may be immersed in the case of dry plates. When sufficient detail has made its appearance, the excess of developer is washed off by a stream of water.

*Intensification of wet plates.* When the density of the negative is not sufficient for printing purposes, it may be strengthened by pouring over the plate a sufficient quantity of either of the following solutions:

	a	b
Pyrogallol	10 grs.	—
Citric acid	20 grs.	50 grs.
Ferrous sulphate	—	25 grs.
Water	5 oz.	5 oz.

After the plate has been thoroughly moistened with the solution, the latter is poured back into the developing-glass and a few drops of a 10-grain solution of silver nitrate added to it. On re-flooding the plate with the mixture, the image will gradually gain in density. Other substances may be employed as intensifiers, some of which will be mentioned in connection with dry plates, but for a full description of the various formulæ text-books on photography must be consulted.

*Fixing.* To remove the unacted-upon silver salt, so-called, potassium cyanide may be used, being contained in a flat dish, or in an upright bath provided with a dipper. The following quantities are those generally employed for plates—

	a
Sodium thiosulphate	4 oz.
Water	20 oz.

<sup>1</sup> The insoluble barium sulphate formed is filtered off; b is suitable for positives.

Potassium cyanide.	120 grs.
Water	5 oz.

a is preferred for negatives, b for positives. Great care is required in the employment of the latter salt on account of its very poisonous character.

*Varnishes.*—For the protection of films they should be covered with a coating of varnish as clear and as hard as possible, to prevent damage during the printing. These varnishes are in such solvents as alcohol, benzene, or chloroform. The composition of some of these is kept secret, but the quantities given in the next column yield good material for ordinary work.

a and c are suitable for negatives, c being very hard and durable. b may be rubbed off for retouching the negative, and should not be used when great permanency is required. For further details with regard to photographic varnishes v. VARNISH.

—	a	b	c	d
Shellac	150 gr.	—	—	—
Sandarac	150 „	384 gr.	—	430 gr.
Mastic	60 „	—	—	—
White hard varnish	—	—	3 oz.	—
Camphor	3 gr.	—	—	—
Oil of lavender	—	5 dr.	—	1 dr.
Chloroform	—	2 „	—	—
Oil of turpentine	½ dr.	—	—	3 dr.
Venice turpentine	½ dr.	—	—	—
Alcohol	5 oz.	5 oz.	5 oz.	5 oz.

#### DRY PLATE PROCESSES.

*Collodion emulsion.* Next to the wet plate process come the more modern or emulsion processes, which may conveniently be divided into those containing collodion, and those containing gelatin, the latter being a thickening medium in the emulsion. Gelatin emulsions are now the most important; but, the others being useful for certain purposes, the collodion emulsion is briefly described, proceeding to those in which gelatin is employed.

The plates having been prepared and edged, if necessary, as previously described, may be coated with an emulsion prepared in the following manner. The plain collodion may be made by dissolving 200 grains of ordinary pyroxyline in 5 ounces of alcohol (sp.gr. 0.820) mixed with 10 ounces of ether (sp.gr. 0.730). To make, say, 1 pint of emulsion from this, after the final treatment of emulsification, drying, washing, and re-emulsifying has been gone through, we may take 7½ ounces, or the half of the collodion prepared. 200 grains of zinc bromide are next weighed out in two portions of 100 grains each, one of these portions being dissolved in the smallest quantity of alcohol; 4 or 5 drops of nitric acid are added to the solution, and then poured into the collodion. The second 100 grains are dissolved in a boiling tube in alcohol, 10 drops of nitric acid added, and kept ready for use. Next 330 grains of silver nitrate are weighed out and dissolved in about 5 to 6 drs. of water, and 10 drops of nitric acid added to the solution. To

this solution  $1\frac{1}{2}$  ounces of warm alcohol are added, and the two liquids thoroughly mixed. The collodion containing the zinc bromide is now placed in a vessel convenient for mixing, and the solution of silver nitrate gradually added, with constant stirring, till about one-half to three-quarters of the silver solution has been poured in. The whole of the bromide solution is now added in exactly the same way as described, and then the remainder of the silver solution. Should any of the silver solution crystallise on the sides of the boiling-tube it may be dissolved in a little water and about half an ounce of alcohol, and added to the emulsion with constant stirring. The emulsion so prepared, when examined by a candle or gas flame, should appear of a deep orange tint by the light transmitted through a thin film.

*Manufacture of gelatin emulsions.* Gelatin emulsions are now so varied in their nature and the details of their preparation are so carefully guarded by the proprietors, that it is impossible here to deal with the details of their preparations. Only a short description is given, therefore, of the general points in the manufacture of an emulsion on a small scale.

Gelatin emulsions may be arranged in the following three classes: (a) the ammonio nitrate process, (b) the acid boiling process, and (c) the cold process. (a) is simple, easy to perform and suitable for beginners; (b) requires more apparatus and does not yield quite so sensitive an emulsion; (c) requires no heating but is apt to yield irregular results.

It is necessary that all operations in making the emulsion be done to obtain the required rapidity, and finally washing the emulsion when formed—should be carried out in the dark room or in red light. For most cases, light passing through ruby glass is sufficient, but in the manufacture of extra rapid emulsions greater precaution with regard to light is necessary. As during the process of manufacture the emulsion must be kept at a certain temperature, glass or porcelain vessels are necessary for dissolving and mixing the constituents, and a small pan or dish is required for keeping these vessels at the required temperature by hot water.

The substances required for a simple emulsion are silver nitrate, potassium bromide, and auto-type, or hard gelatin, in quantities for a small amount of emulsion are obtained by taking 300 grains of gelatin, cut up into shreds by scissors. These are transferred to a glass beaker, or other vessel, and covered with 5 ounces of water, in which 185 grains of potassium bromide have been dissolved. By a little stirring in a glass rod the gelatin gradually softens and swells. While the gelatin is being softened, 231 grains of silver nitrate are dissolved in 5 ounces of water by gentle heat in the pan or water-bath, and when the solid is thoroughly dissolved some strong solution of ammonia (0.880) is gradually added to the silver solution, with constant stirring, until the precipitate which first forms is dissolved. The two vessels are now placed in a pan with water, kept rigorously at a temperature never rising above  $35^{\circ}$  until the gelatin becomes first viscous, and then, with constant stirring, perfectly liquid. It is essential that the gelatin be perfectly liquid before adding the silver salt.

Up to this point the operations may be carried out in the ordinary light, but all further work must be done in ruby light.

When the gelatin is thoroughly liquefied the solution of silver nitrate is added gradually. Many arrangements have been suggested for this purpose, but the best is to time for the proper addition of the silver solution to the gelatin, but it can be done with ease by pouring the solution in a thin stream from an ordinary lipped beaker, or through a glass funnel with a very small orifice. When the mixture is complete, wash out the rest of the silver solution remaining in the beaker with about an ounce of warm water, and add to the emulsion. The emulsion must now be examined by spreading a little on a glass plate and looking at it by transmitted light, when it should appear of a violet colour, apparently with a tendency to assume a rose-pink tinge. The emulsion having been allowed to remain in the hot water for from half to three-quarters of an hour to undergo a process of ripening, is then poured into a flat dish, and placed in a perfectly dark room to set. It should remain thus for at least 24 hours, but will be better if allowed to remain two or three days. As the emulsion when first prepared contains an excess of silver salt, it must undergo a process of washing, which may be carried out in ruby light in two ways.

The gelatine pellicle, having been scraped off from the dish by a bone or glass spatula, is transferred to a square of coarse canvas, thoroughly wetted to soften it. The corners of the square are gathered together and tied with string, thus inclosing the pellicle in a rough bag. This bag, containing the pellicle, is placed in a vessel of water, and thoroughly kneaded by squeezing it against the sides of the vessel by means of the hands. The water is thus squeezed in, and the whole of the water is poured off and the pellicle again covered with fresh water, allowed to stand for about 5 minutes, and the water again poured off, this operation being repeated six or eight times. It will be found advantageous during the washing to tease up the shreds of the pellicle by a tap and running water can be obtained, the washing will be facilitated.

After perfect washing the pellicle is turned out of the washing jar on to a porcelain strainer, covered with a handkerchief, and the excess of water drained away. It may then be swilled with a wash of methylated spirit, which facilitates drying, and transferred by the porcelain spatula or glass spoon to a suitable jar covered with a lid, until it is required for coating the plates. Other methods of washing the pellicle have been introduced, such as placing it on a hair sieve after squeezing through canvas, and then washing on the sieve in a stream of water from the rose tap. It is possible that spreading the emulsion on a sieve facilitates the subsequent drying.

A second method of washing the emulsion and removing the soluble salts is to precipitate it with alcohol. This is done by pouring warm methylated spirit into the emulsion, with constant stirring, when, on allowing the

mixture to cool, the emulsion is found precipitated at the bottom of the vessel. The precipitated emulsion can then be washed in a stream of water, and transferred to a covered pot until required for coating the plates.

The numbers just given will be found convenient for a beginner making an emulsion for

the first time, and yield one of moderate rapidity. The following table gives a selected series of emulsions suitable for different purposes. Nos. I. and II. are of different degrees of rapidity, the first yielding a material suitable for use when no great rapidity is required; the second deals with an emulsion of greater sensitiveness.

TABLE OF VARIOUS GELATINO-BROMIDE EMULSIONS.

	I.	II.	III.	IV.	V.	VI.
A { Silver nitrate . . . . .	200 grains	200 grains	400 grains	200 grains	330 grains	462 grains
Distilled water . . . . .	3 ounces	3 ounces	7 ounces	3 ounces	3 ounces	10 ounces
Ammonia (.880) . . . . .	—	—	{ sufficient to dis- solve ppt. }	—	—	{ sufficient to dis- solve ppt. }
Ammonium iodide . . . . .	—	—	24 grains	—	—	—
Ammonium bromide . . . . .	—	—	280 grains	120 grains	200 grains	—
Potassium bromide . . . . .	160 grains	165 grains	—	—	—	370 grains
B { Gelatin (Nelson's No. 1) . . . . .	40 grains	30 grains	80 grains	30 grains	218 grains	615 grains
Hydrochloric acid (1 p.c. sol.) . . . . .	200 mins.	—	—	—	—	—
Distilled water . . . . .	2½ ounces	2½ ounces	5½ ounces	4 ounces	3 ounces	10 ounces
C { Potassium iodide . . . . .	12 grains	6 grains	—	—	—	—
Distilled water . . . . .	½ ounce	½ ounce	—	—	—	—
D { French gelatin . . . . .	—	—	—	—	218 grains	—
Hard gelatin . . . . .	300 grains	250 grains	—	200 grains	—	—
Water . . . . .	4 ounces	3 ounces	—	—	3 ounces	—
E { Methylated spirit . . . . .	—	—	2½ ounces	—	—	—
Salicylic acid . . . . .	—	—	25 grains	—	—	—

For more detailed information regarding the manufacture, ripening, &c., of gelatin emulsions the various text-books on photography must be consulted.

For coating gelatinized plates with emulsion on a small . . . . . method may be employed. The plate must be laid on a very . . . . . stand or tripod. A quantity of emulsion sufficient to cover nearly half the plate is poured on the middle of it; a glass rod about 2 ins. longer than the width of the plate is then grasped between the fingers and thumbs of both hands, dipped across the plate, into the middle of the pool of emulsion, and steadily moved first to one end and then to the other of the plate. By a motion of the finger and thumb the rod can be raised a slight distance from the plate, so as to allow the emulsion to coat smoothly, and, by resting the tips of the finger and thumb upon the levelled slab, a guiding motion may be given to the rod. In the large manufactories many mechanical arrangements are employed to facilitate rapid coating of the plates.

When the emulsion is thoroughly set on the plates, they are removed from the level slab to a suitable rack to undergo a thorough drying process. This is most conveniently done in a . . . . . drying-box with a current . . . . . from the outside passing through it. The artificial heating of the air is unnecessary if the air-passages are sufficiently large and properly arranged.

The plates will take from 12 to 48 hours to dry, according to circumstances, and may then be packed until required for use.

*Ortho-chromatic photography.* On comparing the curves indicating the intensities of the visual and the photographic rays, it will be at once observed . . . . . exists between them, the visual intensity being greatest about the points D and C, and the photographic intensity about the point G in . . . . . gra . . . . . to the . . . . . Fa . . . . .

*Ortho-chromatic photography* is by . . . . . dyes introduced into the sensitive material to bring the visual and the photographic intensity as much into harmony as possible. This unison may be partially brought about by the introduction into the photographic film of substances such as eosin, erythrosin, rose of Bengal, cyanin, &c.

The most important work in the direction of ortho-chromatic photography has been carried out by Becquerel, Eder, and Vogel on the continent; Cary Lea in America, and by Alney, Waterhouse, and C. H. Bothamley in this country. The dyes are now generally incorporated with the sensitive film, but may also be used in the form of screens placed in close juxtaposition to the plate.

The amount of dye employed must be small, as the effect is destroyed by large quantities. When mixed with the emulsion it is generally found best to employ about 15-30 min. for every 500 c.c. of emulsion; but when the sensitive plate is dipped in the dye a solution of 1 part of dye in 20,000 of water is sufficient.

Orthochromatic plates may be divided into (1) those sensitive to the green and yellow rays, (2) to orange and red rays, and (3) to the entire

spectrum (panchromatic). There are many sensitive substances employed, but the following table shows some of those most commonly used :—

		a	b	c
I.	Erythrosin	10 grs.	—	—
	Cyanine blue (ethyl cyanine or pinacyanol)	—	1 gr.	—
	Auracine	—	—	1 gr.
	Alcohol	4 oz.	8 oz.	—
	Water	—	—	10 oz.
II.	Ammonia (0·880)	1 dr.	—	1 dr.
	Water	24 oz.	—	—

(a) is suitable for the blue-green region, and if the plate be sensitised by dipping, it should be used within a few days. (b) is for the red region. These plates from their sensitiveness must be prepared practically in the dark. (c) is for green and blue-green rays. The auracine is dissolved in boiling water, filtered, and the ammonia added to the cooled solution. This solution reduces the speed of the plate.

For panchromatic plates the two following solutions may be used : (d) alcoholic solution of pinachrome (1:1000); ammonia (0·880), 5 min.; water, 1 oz.; (e) alcoholic solution of homocol (1:1000); ammonia, 10 min.; water, 1 oz.

Special care must be taken in preparing these plates, which should be done somewhat quickly, and in the dark.

Many other sensitisers may be used, of which the following are instances. For blue-green and green, acridine orange without ammonia. For green and yellow (but not red) erythrosin as above. Green, yellow and red, orthochrome, pinaverdol, pinachrome or homocol. Extreme visible red, pinacyanol. Infra-red, dicyanine.

The following curves, taken from Bothamley's papers on this subject, show the increased sensitiveness produced by some of these dyes in the portion of the spectrum lying between A and E :—

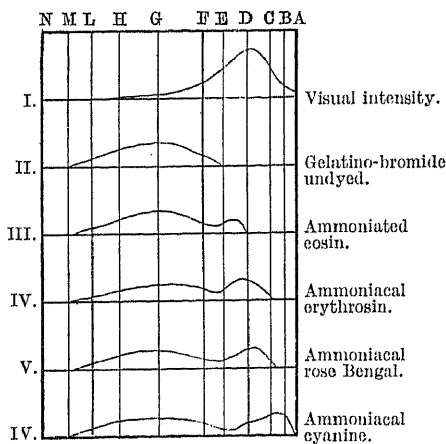
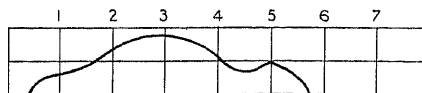


FIG. 6.

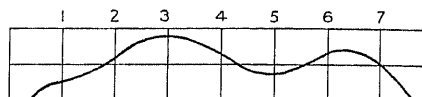
The following diagrams indicate the increased sensitiveness of (a) an isochromatic plate showing

partial sensitiveness; and (b) a panchromatic plate with the sensitiveness extending into the red rays.



Spectrum of Isochromatic Plate

FIG. 7(a).



Spectrum of Panchromatic Plate

FIG. 7(b).

The chief use for plates so sensitised will be found in the copying of pictures, flowers, or distinct patterns of different colours, where as much harmony as possible is required between the visual and photographic effect, but they will also prove useful in high-contrast contrasts sometimes found in nature.

For detailed information on ortho-chromatic photography special papers relating to the subject should be consulted.

#### DEVELOPMENT OF DRY PLATES.

The development of dry plates produced either by collodion or gelatin emulsion is carried out either by iron-salts—such as ferrous oxalate or ferrous citro-oxalate—or by what is termed 'alkaline development,' in which pyrogallol, hydroquinone, amidol, or some other

and with ammonia, or the carbonates of potassium or sodium, as accelerators of the reducing action.

*Development with ferrous oxalate.* This method is simple for ordinary dry plates, and may be employed for negatives on paper, or enlargements on gelatino-bromide paper, but it does not permit correction of inaccurate exposure to such an extent as the pyro-developer. The ferrous oxalate developer may be prepared by adding 1 volume of a saturated ferrous sulphate solution to 4 volumes of a saturated solution of potassium oxalate. Such solutions are obtained by dissolving 4 oz. of neutral potassium oxalate and 6 oz. ferrous sulphate separately each in 10 oz. of water. A solution of potassium bromide, containing 20 grs. bromide to the oz. of water, should also be made; of this, about 1 dr. may be taken for every 2½ oz. of ferrous oxalate developer is specially applicable in the development of transparencies or positives made with gelatino-chloride or collodio-chlorido emulsions. It is, however, generally found better for this last-named emulsion to employ a ferrous-citro-oxalate, or ferrous citrate developer, with which, by varying the amount of the potassium bromide solution, various tones may be given to the prints. The quantities given in the following table may be regarded as good standard quantities to be selected from :—

*For Transparencies.*

		<i>a</i>	<i>b</i>
I.	Potassium oxalate . . . . .	5 oz.	2 oz.
	Ammonium chloride . . . . .	—	40 grs.
	Citric acid . . . . .	—	—
	Water . . . . .	20 oz.	20 oz.
II.	Ferrous sulphate . . . . .	5 oz.	240 grs.
	Sulphuric acid . . . . .	30 mm.	—
	Citric acid . . . . .	—	120 grs.
	Alum . . . . .	—	120 grs.
	Water . . . . .	20 oz.	16 oz.

With (*a*) mix 1 oz. of I. with 3-4 oz. of II., pouring II. into I. To obtain black tones with (*b*) use equal proportions of I. and II. The solutions when mixed may be used for several plates in succession.

Development by ferrous oxalate or ferrous-citro-oxalate is simpler than with alkaline pyrogallate, but greater attention must be paid to the exposure, as there is less power of working up an under-exposed plate.

*Alkaline development.*—In this development the pyrogallol gives density, the soluble bromide is supposed to act as a restrainer, and the ammonia or alkaline carbonate as an accelerator. The pyrogallol may be kept in the dry condition and added to the developer when required, but it is customary to keep all the substances as separate stock solutions. For perfect work it is therefore better to keep the three ingredients separate, but the stock solutions may be reduced to two in number, and even a single stock solution may be used. In this latter case, however, the operator has not so much control over the retardation or acceleration of the development in cases of incorrect exposure. The amount of pyrogallol generally employed varies from between 1 grain to 5 grains per fluid ounce of developer, and full details of the correct quantities are almost universally given with the plates supplied by the different makers.

*Developing solutions for gelatino-bromide plates.* The following may be taken as instances of standard forms of developers. The solutions should preferably be kept separate, at least the organic developer should not be mixed with the alkali till required for use. I. may be termed

the developer; II. the accelerator; and III. the restrainer, to be used in quick succession. The following developers with pyrogallol are given as types of the two and three solution developers.

		<i>a</i>	<i>b</i>
I.	Pyrogallol . . . . .	1 oz.	$\frac{1}{4}$ oz.
	Nitric acid . . . . .	—	5 min.
	Citric acid . . . . .	40 grs.	—
	Water . . . . .	$7\frac{1}{2}$ oz.	20 oz.
II.	Ammonia solution (0-880) . . . . .	1 oz.	—
	Sodium sulphite . . . . .	—	$2\frac{1}{2}$ oz.
	Sodium carbonate . . . . .	—	2 oz.
	Potassium bromide . . . . .	120 grs.	—
	Water . . . . .	7 oz.	20 oz.
III.	Potassium bromide . . . . .	—	$\frac{1}{4}$ oz.
	Water . . . . .	—	2 oz.

(*a*) In separate bottles take 1 part of No. I. and of No. II., and to each add 19 parts of water. These should be mixed just before use. To develop when the exposure is correct take equal parts of the diluted solutions.

(*b*) Mix equal parts of Nos. I. and II., and add 10 min. of No. III. to each ounce of the mixed developer. For instantaneous exposures No. III. may be omitted.

The manipulation required in dry plate development is very simple, as the operation is carried out in a dish. The plate, taken from the dark slide, is laid in the developing dish or tray face upwards, and if ferrous oxalate or citrate be used the proper quantity may at once be flowed over the plate, allowing the liquid to run gently from one end of the plate to the other. A gentle rocking motion may be given to the dish during development, so as to change the liquid over the surface of the plate. The image gradually appears, the high lights gaining density first. Complete development may be recognised by a faint image appearing on the back of the negative, or looking through the negative at the red window or lamp, when the plate should show a very complete deposition of silver on the high lights. The knowledge of the exact extent for correct development can only be obtained by practice.

*Table of some of the Common Developers.*

		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
I.	Pyrogallol . . . . .	55 grs.	80 grs.	—	—
	Metol . . . . .	45 grs.	—	—	—
	Hydroquinone . . . . .	—	8 grs.	40 grs.	120 grs.
	Eikonogen . . . . .	—	—	120 grs.	—
	Potassium meta-bisulphite . . . . .	120 grs.	80 grs.	—	—
	„ bromide . . . . .	20 grs.	—	—	60 grs.
	Sodium sulphite . . . . .	—	—	1 oz.	1 oz.
	Citric acid . . . . .	—	—	20 grs.	5 grs.
	Boric acid . . . . .	—	10 grs.	—	—
	Water . . . . .	20 oz.	20 oz.	20 oz.	20 oz.
II.	Sodium carbonate . . . . .	4 oz.	1 oz.	60 grs.	—
	„ hydroxide . . . . .	—	—	30 grs.	—
	Potassium bromide . . . . .	—	—	6 grs.	—
	„ carbonate . . . . .	—	—	—	2 oz.
	Rodinal . . . . .	—	—	—	1 oz.
	Sodium sulphite . . . . .	—	1 oz.	—	—
	Water . . . . .	20 oz.	20 oz.	20 oz.	20 oz.



In many cases the organic developer and the alkaline accelerator may be mixed together in one solution. The following may be taken as typical developers of this class:—

	a	b	c	d	e	f	g
Organic							
Eikinogen . . . . .	120 gr.	—	—	—	—	—	—
Glycin . . . . .	—	160 gr.	—	—	—	—	—
Metol . . . . .	—	—	50 gr.	65 gr.	—	25 gr.	—
p-Aminophenol . . . . .	—	—	—	1½ dr. fl.	—	—	—
Sodium carbonate . . . . .	240 gr.	—	720 gr.	—	75 gr.	18 gr.	—
„ sulphite . . . . .	480 gr.	240 gr.	360 gr.	1440 gr.	840 gr.	360 gr.	480 gr.
Potassium carbonate . . . . .	—	800 gr.	—	—	600 gr.	480 gr.	—
„ bromide . . . . .	—	—	—	—	8 gr.	—	—
„ metabisulphite . . . . .	—	—	—	—	—	—	—
Water . . . . .	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.
Accelerators.							

As a rule these developers should be diluted with an equal quantity of water immediately before developing. With developer (e) for portraits take equal parts of stock solution and water; for landscapes 1 part of stock to 2 of water.

The glycin developer (b) is a slow developer, but particularly suitable for 'stand development.'

In commencing the development of a plate it is better to begin with a less quantity of the accelerator than the full amount stated, and gradually add the remainder as development advances.

The darkening of the film when the alkaline pyrogallol developer is used must not be allowed to go on so long as with the ferrous oxalate developer. In the former case the image is of a slightly yellow tinge, and consequently of a more non-actinic nature than that formed by the oxalate. As has been already stated it is not absolutely necessary that three separate solutions be kept, but it is better so as to facilitate the retardation of development on over-exposure, or its acceleration on under-exposure. If proper exposure has been given the image will appear in about one minute, and gradually gain in density.

When all the details are visible, and apparently stops, a few more drops of the accelerator may be poured into the developing cup, the developer will be fresh, and again flowed over the plate. This fresh addition of the alkali rapidly produces increase of density. When the development is deemed complete, wash thoroughly in a gentle stream of water from the rose-tap and place in the fixing-bath, unless it be deemed necessary to soak the plate in an alum solution for some time.

For the development of dry plates for transparencies, the developers given in the following table will be found useful, and will give different tones to the transparencies:—

*Pyro and Ammonia Developer for Warm Tones.*

I.	Pyrogallol . . . . .	1 oz.
	Sodium sulphite . . . . .	4 oz.
	Citric acid . . . . .	½ oz.
	Water . . . . .	16 oz.
II.	Ammonium bromide . . . . .	1 oz.
	Liquor ammonia (0.880) . . . . .	5½ dr.
	Water up to . . . . .	16 oz.

For use mix 1 part of No. I. with 3 parts of No. II. and dilute to double the quantity with water. The mixed developer may be used for several plates.

#### Developers for Black Tones.

	a	b
Hydroquinone . . . . .	60 grs.	—
Amidol . . . . .	—	80 grs.
Sodium carbonate . . . . .	4 oz.	—
„ sulphite . . . . .	2 oz.	2 oz.
Potassium carbonate . . . . .	2 oz.	—
„ bromide . . . . .	40 grs.	½ oz.
Water . . . . .	20 oz.	12 oz.

These developers may be used for several plates, and will keep good for some time. In almost all cases it will be found best to use the developer which is generally described on the box of the special plate used.

Many operators now prefer a fixed time development during which the plate if properly exposed need not be examined. This is carried out in a closed box or tank, of which many forms are on the market. Tables are also given by which the time necessary for different developers may be calculated.

*Intensification and reduction of dry-plate negatives.* If proper exposure be given to the plate the process of development by the ferrous salt or by pyrogallol will always yield sufficient printing density. Both under- or over-exposure, however, will yield an image far too thin to give a vigorous and brilliant print. This deficiency may be remedied to a certain extent by the process of intensification; but it must be understood that the results, when such a process has to be employed, are never so brilliant as with a properly-exposed and properly-developed negative.

Several methods are in general use for the intensification of dry plates, one of the most usual being that in which the action is carried out by a mercury salt and ammonia. In dry plate work the process of intensification is almost invariably carried out after fixing. For this purpose it is necessary that the last traces of sodium thiosulphate should be removed from

the negative by thorough washing. Should it be necessary to take still further precautions for the removal of the last traces of thiosulphate, the negative should be soaked in a saturated solution of alum containing 3 grains of citric acid to the ounce of solution, or in a solution of hydrogen peroxide containing 1 drachm of 'hydrogen peroxide solution' to 5 oz. of water. The plate may be soaked in these from 10 to 30 minutes, and again washed before intensification.

To intensify, first thoroughly soak the plate in water to soften the film, then place in the following solution, preferably in a black vulcanite dish:—

## I.

Mercuric chloride . . . . .	200 grs.
Ammonium chloride . . . . .	200 grs.
Water . . . . .	10 oz.

The plate rapidly undergoes a process of bleaching, and when the film is bleached throughout it is removed from the solution and thoroughly washed under the tap. The washing in this case must be most thorough. After this washing the plate is flooded with a solution of ammonia:

## II.

Ammonia, 0.880 . . . . .	1 part
Water . . . . .	10 parts

In this solution the plate rapidly assumes density, becoming changed first to a rich non-actinic brown, and finally to black, according to the length of time it has been left in the mercury bath.

The plate may also be intensified by one or other of the following solutions:—

—	a	b	c	d
Sodium sulphite	1 part	—	—	—
Ferrous oxalate	—	ordinary developer	—	—
Hydroquinone . . . . .	—	—	ordinary developer	—
Uranium nitrate	—	—	—	1 part
Potassium ferricyanide . . . . .	—	—	—	1 "
Acetic acid (glacial)	—	—	—	10 parts
Water . . . . .	6 parts	—	—	100 "

(a), (b), and (c) are to be used after the negative has been bleached by the mercuric chloride solution; (d) is an intensifier by itself.

In all cases the plates should be well washed between the application of solutions I. and II. and after intensification; they may also be placed in the fixing bath again for a minute or two with advantage, and then finally washed.

*Reducing negatives.* Should the negative after development and fixing appear too dense for printing purposes, one of the following courses of treatment will cause its reduction:—

(1) Soak the plate carefully in sodium thiosulphate solution (2 oz. to 1 pint) to which has been added potassium ferricyanide sufficient to give it a yellow colour. The reduction in this case takes place with considerable rapidity, and a stream of water or a washing dish should be handy for immersion of the negative to check too rapid reduction.

(2) Immerse the moist negative in one of the following solutions:—

—	a	b	c	d
Potassium ferric oxalate	150 grs.	—	—	—
Sodium sulphite . . . . .	125 "	—	—	—
Oxalic acid . . . . .	45 "	—	—	—
Sodium thiosulphate . . . . .	1½ oz.	—	—	—
Ammonium persulphate . . . . .	—	15 grs.	—	—
Potassium permanganate (10 p.c. solution)	—	—	1 dr.fl.	—
Potassium dichromate	—	—	—	100 grs.
Sulphuric acid (10 p.c. solution) . . . . .	—	—	5 dr.fl.	7 dr.fl.
Water . . . . .	7 oz.	1 oz.	10 oz.	20 oz.

*Fixing the negative.* This operation is performed for dry plates as has already been mentioned, and for wet plates, except that sodium thiosulphate is always employed and not potassium cyanide. The usual strength of the solution is 4 oz. of thiosulphate to 1 pint of water, but this may be varied according to the experience of the operator.

*Transparencies.* When a positive picture is required for enlargement, or for showing on a screen to an audience, it is found more convenient to employ an emulsion of gelatin and silver chloride, alone or a mixture of the silver chloride and bromide. The following quantities may be taken as giving emulsions suitable for this purpose:—

—	I.	II.
Gelatin (Nelson No. 1) . . . . .	300 grs.	80 grs.
Ammonium bromide . . . . .	—	210 grs.
Ammonium chloride . . . . .	100 grs.	—
Sodium chloride . . . . .	—	50 grs.
Hydrochloric acid . . . . .	—	5 mm.
Water . . . . .	10 oz.	10 oz.
Silver nitrate . . . . .	240 grs.	400 grs.
Hard emulsion gelatin . . . . .	—	400 grs.

In No. 1 allow the gelatin to soften and swell in the water; then place all three vessels in a water-bath at a temperature of 120°F. (49°C.). When the gelatin is melted add the silver solution to it, and then stir in the ammonium chloride solution. Allow the emulsion to ripen at that temperature for an hour, and pour out into a dish for setting. The details of washing, coating, and drying the plates, are the same as for the bromide emulsions already described.

As the film left by gelatino-chloride plates after development and fixing is extremely clear in the high lights, it is necessary for these plates to employ glass perfectly free from flaws or air bubbles.

Gelatino-chloride plates are less sensitive to light than the bromide plates, so that for contact transparencies from well-defined negatives, the exposures are proportionately longer.

These plates may be developed by potassium ferricyanide, or by the mixture of potassium ferricyanide and citrate previously mentioned, or by the hydroquinone developer.

Gelatino-bromide plates also yield good transparencies, but if they are used for this purpose a fairly strong pyro-developer should be taken and the development carried out quickly.

*Transparencies* are now commonly made by the carbon process (v. Carbon processes).

Formulae useful in the development of transparencies are described under the development of

or celluloid films. In the early sensitive—that introduced by Fox Talbot—the material employed as the substratum for the sensitive film was paper instead of glass. Although the employment of glass as a support to the sensitive film became generally adopted when the collodion process was perfected by Archer in 1852, paper and particularly celluloid material have again come into use. This reintroduction of paper as a basis for the sensitive film is due in a great measure to Messrs. Woodbury and Warnerke, who have acted as pioneers in this, and in the design of apparatus necessary for the manipulation of such coated surfaces.

The details of coating such films with the emulsion are nearly allied to those of coating the glass plate. The actual difference between the two methods consists in the special manner in which the sensitive films are arranged in the camera for exposure. This may be done in two ways. The film, if sufficiently rigid, may be cut into definite sizes the same as the glass plates, and then fixed by specially-constructed slips of thin wood or metal in the ordinary dark slides exactly in the position that would be taken by the glass plate. Another method is to suspend the sensitive paper in a continuous roll in what is termed a roller slide, which takes the place of the dark slide containing the sensitive plate. In this arrangement the continuous slip may be rolled off from one spool to another across the camera, a mechanical check or signal being given as soon as the length of paper corresponding to the width of the camera has passed over, thus placing a fresh surface in position before the lens. The process may be repeated until twelve or more portions of the continuous film have been exposed. The film may then be removed from the dark slide for development, and another roll placed on the rollers in the slide.

The development of such films may be carried out with the same solutions as those employed for glass-plate development. Should the film be thick enough they may be treated as glass plates, but under ordinary circumstances the films now used are too thin for such treatment and are best developed as a whole film. For this purpose the film may be attached to a roller or wheel which can be rotated in the developer; or the film may be held at each end by the hand and passed through the developer backwards and forwards with the sensitive side downwards, being kept down in the developer by a porcelain bridge standing in the developing dish. It will be found advantageous to soak the paper in water before development until all tendency to curl up has disappeared. Retardation or acceleration of the development may be done in the same manner as for glass plates.

Various appliances, such as developing tanks, have been introduced of late years for the development both of plates and roller films, which have removed many of the difficulties originally experienced by beginners in the manipulation of films.

The use of bromide emulsion paper for printing purposes is dealt with under *Silver printing*.

### SILVER PRINTING.

Printing on paper with silver salts may be arranged under the following three sections:—

- (1) Printing on sensitised albumen paper;
- (2) Printing in sunlight with gelatino chloride emulsion paper (printing out paper);
- (3) Printing in artificial light with gelatin bromide emulsion, and afterwards developing.

The paper coated with albumen or gelatin is first treated with a solution of some soluble chloride, such as ammonium chloride, so that when brought in contact with a solution of silver nitrate its surface may be sensitised with the mixture of silver chloride and free silver nitrate. In the action of the light through the negative upon the sensitive paper a gradual darkening takes place during the decomposition of the chloride and albuminate of silver, and a copy or positive of the negative is produced, the lights and shades of the original object being truly represented. In ordinary silver printing the action of the light is allowed to proceed to such a length as to produce an image slightly darker than the print required, as the operations of toning and fixing have a tendency to weaken the colour of the print. At the present time albumenised paper has largely been replaced by papers coated with gelatin-chloride emulsions sold by makers as printing out papers (P.O.P.). As albumenised paper, however, is still employed in certain cases, and as the method of further treatment with it and with P.O.P. papers is very similar, a short description is given of its preparation.

As the albumen is removed from the immediate action of a fixing agent on the silver compounds is a disagreeable red, the print undergoes the process of toning, which is effected by immersing it in a solution of gold, containing some substance capable of removing the chlorine derived from the albumen and the silver sub-chloride produced by the action of the light. After sufficient tone of a brown or purple kind has been imparted to the print, the unacted-on silver compound is removed by sodium thio-sulphate in the same way as with the wet plate.

To prepare albumenised paper, coat with the following:—

Albumen (white of egg)	10 oz.
Ammonium chloride	100 grs.
Spirits of wine	$\frac{1}{2}$ oz.
Water	3 oz.

Dissolve the chloride in the water and spirits of wine, then add the white of egg solution, with constant shaking for about half an hour, or, better still, break up the cellular membrane by mechanical stirring. Filter through a sponge or glass wool into a flat dish.

For plain salted paper the following quantities may be taken:—

Ammonium chloride	30 <sup>a</sup> grs.	50 <sup>b</sup> grs.
Sodium chloride	15 grs.	
Sodium citrate	50 grs.	
Gelatin	5 grs.	5 grs.
Distilled water	5 oz.	5 oz.

Dissolve the gelatin in the water, then add the other substances, and filter.

To coat the paper the sheet must be held carefully by two corners, gently bent back, and

the middle of the convex side of the sheet lowered on to the solution in the dish. After 2 to 3 minutes raise, and again lower, to avoid air bubbles. Float on the solution for 2 to 5 minutes, then hang up to dry.

*To sensitise the paper.* A silver solution, stronger than that used for sensitising the plate must generally be employed. The following give varying strengths for different circumstances:—

Silver nitrate	50 grs.	80 grs.	30 grs.
Water (distilled)	1 oz.	1 oz.	1 oz.

*a* may be used for ordinary cases, *b* where the negative is weak, and *c* where the lights and shades on the negative show great contrast. The strength of the bath becomes gradually lowered, and must be restored from time to time. Only strong negatives should be printed in direct sunlight; all other cases should be exposed only to diffused daylight or covered with tissue paper or ground glass d.

*Toning.* To colour of the printed image, it is immersed in a neutral solution of gold containing certain metallic salts. The following are some selected toning baths:—

—	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Gold chloride	1 gr.	1 gr.	1 gr.	1 gr.	1 gr.
Sodium acetate	30 grs.	—	—	—	—
" phosphate	—	20 grs.	—	—	—
" bicarbonate	—	—	30 grs.	—	—
" borate	—	—	—	20 grs.	—
(borax)	—	—	—	—	20 grs.
Water	10 ozs.	10 ozs.	10 ozs.	10 ozs.	10 ozs.

*a* is a good bath for ordinary use, giving purple-brown tones, but should be made up 12 hours before use; *b*, *c*, and *d* can be used shortly after making, and give purple tones, but do not keep well; *e* gives fine purple-brown tones, and keeps fairly well in the dark. These solutions may also be made up in strong solutions by dissolving the tube of 15 grs. of gold in 15 oz. of water, and adding the proper quantity of alkaline salt. To make the bath for immediate use mix 1 part of the stock solution with 10 oz. of water.

The chemical reactions taking place in the process of toning do not appear to depend on their nature, the tone being:

film of gold, reduced from a neutral solution of gold chloride ( $\text{AuCl}_3$ ), or of the double salt ( $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ ), upon the film containing the reduced products from the silver chloride and albuminate. To obtain the best results the gold solution must be neutral or very slightly alkaline.

*Fixing the print.* This is done by immersing the print, after toning, in a solution of sodium thiosulphate, 4 oz. in 20 oz. of water. This strength is suitable for prints from strong negatives, but where the print is weak the fixing bath may be reduced to 3 or 2 oz. of thiosulphate to the pint of water. Before fixing, the prints should be immersed in water containing a small quantity of sodium carbonate for 10 minutes, and then placed face downwards in the fixing bath. Their brilliancy will at first diminish, but

will to a certain extent be restored when they are finally fixed and dried. The prints should remain in the fixing bath from 10 to 15 minutes, being gently moved about to prevent them sticking together. The prints must be washed after fixing for at least 24 hours in different changes of water, or for 6 in running water.

In silver printing the toning bath should be neutral or . . . and not below  $60^\circ\text{F}$ . The prints must be printed rather darker than finally required, and toned to a chestnut brown, or purple.

*Printing with gelatino-chloride emulsions.* More rapid printing may be effected by the use of a chloride emulsion on paper, as the copy may either be printed to the full extent in a bright light, or the image if imperfectly printed may be fully developed as in the case of a plate or film transparency. The following gelatino-chloride emulsions will be found useful for such papers.

Gelatin	340 grs.	Nelson's No. 1	87 grs.
Ammonium chloride	11 "	Coignet's	87 "
Alum	15 "		18 "
Rochelle salt	15 "		50 "
Water	6 1/2 oz.		
Silver nitrate	115 "		75 "
Citric acid	62 "		
Alcohol			4 drs.
Water	1 oz.		5 oz.

*Rapid printing with gelatino-bromide paper.* Paper coated with gelatino-bromide emulsion is also largely used for printing by artificial light and for purposes . . . The materials and details for coating are much the same as described for the manufacture of plates or films on celluloid.

The exposures may be made by artificial light. After exposure the prints may under general conditions be developed, if necessary, intensified, or reduced, and finally fixed by the solutions already mentioned for bromide plates or films. If desired they may be toned by the gold or platinum solutions already given under *Toning* formulæ, and other colours may be given to them by the use of certain salts. Thus dark brown to red tones may be obtained by using copper salts; green tones by mixed vanadium and iron salts; and blue tones by iron salts. For the development and subsequent treatment it is best to use the special formulæ generally issued by the makers with the different varieties of papers. Should a combined toning and fixing bath be not used, the prints, after toning, must be fixed in the usual way.

The tone of these prints is distinctly neutral and somewhat like platinum prints. The print may be obtained dull by allowing it to dry on blotting paper after final washing, with the sensitised side upwards, or it may be obtained with a glossy appearance by being 'squeegeed,' face downwards, on a glass or ferrotype plate and allowed to dry in that position. When dry, it may be stripped from off the plate.

The printing, like that with albumenised paper, should be carried slightly further than the shade finally required, as the prints diminish in intensity during toning and fixing with certain baths.

*Some Toning Baths for Gelatino-chloride and Bromide Papers.*

—	a	b	c	d	e
Gold chloride	2½ grs.	2½ grs.	5 grs.	—	3½ grs.
Potassium chloroplatinate	—	—	—	4 grs.	—
Citric acid	—	—	—	45 grs.	70 grs.
Borax	90 grs.	—	—	—	—
Sodium acetate	90 grs.	—	360 grs.	—	—
Ammonium thiocyanate	—	90 grs.	35 grs.	—	240 grs.
Alum	—	—	—	—	70 grs.
Lead nitrate	—	—	—	—	90 grs.
Lead acetate	—	—	—	—	90 grs.
Sodium thio-sulphate	—	—	—	—	5 oz.
Water	20 oz.	20 oz.	20 oz.	20 oz.	20 oz.

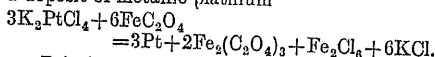
(c) should be made up some time before using, and, if sodium tungstate instead of acetate be used, gives rich chestnut tones. (e) is a combined toning and fixing bath.

The toning must be carried further than in ordinary printing, and the prints may be fixed with thiosulphate directly after toning, without any intermediate soaking in water. In all silver printing processes care should be taken to thoroughly remove the last traces of the fixing agent, and the prints should invariably be thoroughly washed before drying and final mounting.

#### PRINTING IN PLATINUM.

*Platinotype.* This method of printing was introduced by Mr. Willis. It may be divided into three distinct processes. In the first the paper is sensitised with a mixture of ferric oxalate and the platinum salt, and, after exposure, is developed with a hot solution of potassium oxalate. In the second there is no platinum salt on the paper, but it is coated with ferric oxalate containing a small quantity of mercuric chloride, and, after exposure, is developed by a cold solution of potassium oxalate with the platinum salt. The third process differs from the first two in containing both the sensitive material and the developer on the paper during the operation of printing. It is, therefore, like silver printing, a printing process, in which the image is carried to the paper during its exposure to the light, the print requiring no further development after exposure, but merely fixing.

In these processes the action of the light effects the reduction of the ferric to ferrous oxalate  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 = \text{Fe}_2(\text{C}_2\text{O}_4)_2 + 2\text{CO}_2$ , leaving the potassium chloroplatinate un-reduced in the film. On developing the partially-formed image, however, by warm potassium oxalate the ferrous oxalate becomes dissolved out of the film, and at the moment of its solution reduces the platinum salt, thus increasing the image by a deposit of metallic platinum



*Printing with hot developer.* In this case the paper is coated with a mixture of ferric oxalate and potassium platinoous chloride. As there is an intimate mixture of the reduced iron salt with the platinum salt on the surface of the print, when this is floated on a warm solution of potassium oxalate the ferrous salt at once undergoes solution, but in passing into solution it reduces the platinum salt, and a deposit of

metallic platinum is formed, varying with the amount of ferric oxalate reduced, which differs according to the amount of action of the light on the different parts of the plate. On the high lights the ferric oxalate remains unchanged, and therefore no reduction of platinum will take place on these during development.

The paper may be prepared by brushing it over with a saturated solution of ferric oxalate, containing 60 grs. of the platinum salt to the ounce of solution. It is necessary that the paper, after it is coated, should be kept absolutely dry: this is best effected by storing it in tin boxes with lumps of calcium chloride in a perforated chamber at one end of the tin. The amount of exposure requires perhaps greater experience than in silver printing, as allowance has to be made for the circumstance that the image on the paper before development is not sufficiently marked to guide the operator in determining the length of exposure without considerable experience. Proper exposure may be said to have been given when the shadows of the picture are distinctly seen of a drab colour.

For the further development of the image the print is floated face downwards, or drawn over a hot saturated solution of potassium oxalate in the manner previously described for albumenising paper. A solution of the proper strength may be made by dissolving 2½ oz. of neutral potassium oxalate in 10 oz. of distilled water, which should be used in a dish of enamelled iron and kept at a temperature of 170°–180°F. When development is deemed complete, and the full detail of the picture is out, the print is transferred to a solution of hydrochloric acid, of a strength of 1 oz. hydrochloric acid to 60 oz. of water, in which it should remain 10 minutes. The print must then be thoroughly washed in at least three changes of water. Should the prints be deemed over-exposed, the temperature of the developer may be lowered.

The prevailing tone of platinum prints is grey, but different tones such as brown, red and even blue may be obtained by using toning baths containing mercuric chloride, uranium nitrate or potassium ferricyanide respectively.

*Development with cold potassium oxalate.* In the second of the processes the paper is first coated with a saturated solution of ferric oxalate containing about 1–1½ grs. of mercuric chloride to the ounce of oxalate solution. After proper exposure, as before described, the print is floated on a solution of potassium oxalate containing potassium platinoous chloride. The development may be permitted in the composition of this developer, but a solution containing 50 grains potassium oxalate to the ounce of water, with about 9–10 grains of the platinum salt, may be taken as a standard quantity to begin with. Warm tones are produced by lessening the quantity of potassium oxalate; cold or grey tones by increasing it.

The development by this method proceeds slowly, and may be stopped at any moment, great latitude being at the same time permitted. When the print is thoroughly soaked with the developer, it may be placed on a sheet of blotting paper, and the developer removed.

*Direct platinum printing without development.* In this process the paper is sensitised with a mixture of the platinum salt with sodio-

ferrie oxalate and sodium oxalate; small quantities of potassium chlorate and mercuric chloride being also introduced under certain circumstances. This method differs from the other two in that the paper contains the sensitive salt and developer upon it from the start, the printing of the image being continued to the extent. Under the influence of light and the moisture in the air, reduction of the platinum salt takes place in the printing frame. The printing must be continued until the picture has the appearance finally required. In moist weather the printing will go on in a very dry weather the printing is apparently stops after a certain intensity has been reached; it will continue, however, to print, if the back of the paper be breathed upon or very gently steamed.

**Fixing the prints.** This is best done by placing the prints in 1 vol. hydrochloric acid and 60-80 vols. water till the high lights appear perfectly white. They should then be washed in several changes of water. The tone given by platinum prints is especially applicable for copying buildings and machinery, but also yields most beautiful effects in portraiture when the proper lighting of the original negative has been attended to.

#### PRINTING WITH IRON SALTS.

Several processes have been brought forward in which the salts of iron may be employed instead of those of silver and platinum, thus rendering the cost of copying large plans or drawings much less expensive.

The reduction of the ferric salts by light was first utilised by Sir John Herschel, who employed ferric ammonium citrate as his sensitive material, the image with a solution of potassium and the different methods now employed are more or less modifications of his original process.

By mixing the ferric salt and potassium ferricyanide together before coating the paper, the print may after exposure be developed by merely washing in water until the washings are colourless. For such a paper the following mixture will be found useful:—

I.	Potassium ferricyanide	200 grs.
	Distilled water	5 oz.
II.	Ferric ammonium citrate	600 grs.
	Distilled water	5 oz.

Dissolve the salts separately, then mix, keep the solution in the dark, and filter before use. The paper, after coating and drying, must be kept for a few days before use. When thoroughly exposed the print should show a bronze colour in the shadows and is developed by soaking in one or two changes of water. The colour of the prints may be improved by soaking after development in a solution of  $2\frac{1}{2}$  p.c. alum and 3 p.c. oxalic acid.

A method for obtaining positive prints from positives may be carried out by sensitising the paper with the following solution:—

I.	Gum arabic	4 oz.	Mix 8 vols. of II.
	Water	20 "	then 5 vols. of
	Ferric ammonium		III. to 20 vols.
II.	citrate	10 "	of I. in small
	Water	20 "	portions with
	Ferric chloride	10 "	constant stir-
III.	Water	20 "	ring.

The paper is sensitised, dried, and exposed in the usual manner. It may be developed by floating in a solution of 1 oz. potassium ferricyanide in 10 oz. of water. After development immerse in a 1 p.c. cleansing solution of hydrochloric acid or 1:25 sulphuric acid (sp.gr. 1.08) for a few minutes, and dry. These methods are especially useful for copying large line drawings or diagrams, but may also be used for ordinary landscape and portrait prints.

In the Kallitype process the paper may be sensitised by a mixture containing 75 grs. of ferric oxalate with 30 grs. silver nitrate to 1 oz. of water. The ferric oxalate is dissolved in the hot water with a grain or two of oxalic acid to assist solution. After filtering the silver is added and the solution kept in the dark.

The following may be taken as developers for this paper:—

	a	b	c
Borax	2 oz.	$\frac{1}{2}$ oz.	—
Rochelle salt	1 $\frac{1}{2}$ oz.	2 oz.	1 oz.
Potassium dichromate (1 p.c. solution)	15-18 drs.	15-18 drs.	8-10 drs.
Water	20 oz.	20 oz.	20 oz.

(a) yields black, (b) purple, and (c) sepia tones. The prints are fixed in a solution of sodium thiosulphate in 20 oz. of water to which 120 min. of ammonia (0.880) has been added.

Numerous papers for printing from negatives by silver, platinum, or other metallic salts can now be used. The formulæ and details necessary for working the individual processes are best obtained from the directions issued by the various makers.

#### DIAZOTYPE.

Under this heading may be classed two processes for printing in colours which may be shortly described in an article on photography. The one devised in Germany is termed *Fear-type* (from the inventor); the other is the *Prinuline process*, introduced in England by Messrs. Green, Cross, & Bevan.

In the *Fear-type* the material is sensitised with a mixture of a diazo compound with a phenol or amine in molecular proportions, dried in the dark and exposed behind a negative. The azo colouring matter is produced in quantities proportional to the amount of light passing through the negative. After printing, the material is dipped in very dilute hydrochloric acid, and finally washed with water. The following table gives instances of some of the mixtures employed:—

	I.	II.	III.
	Parts	Parts	Parts
Sodium toluenediazo-	25	—	—
sulphonate			
Sodium ditolyl-tetra-	—	25	25
sulphonate			
$\beta$ -naphthol	25	—	—
m-Phenylenediamine	—	20	—
Resorcinol	—	—	12
Sodium hydroxide	8	—	16
Water	1000	1000	1000

*Primuline process.*—If primuline be treated with nitrous acid (dil.), it yields diazo-primuline, which forms various colours by combination with different phenols and amines. If, therefore, a surface be dyed with primuline, converted into diazo-primuline, and exposed to light under a negative or pattern, and be then treated with a phenol or amine, an image is obtained, the colour of which is determined by the nature of the developer used.

The material may be dyed in a hot solution of primuline, washed and converted into the diazo compound by a solution of 0.25 p.c. of acidified sodium nitrite. It is again washed, and allowed to dry in the dark. The exposure is regulated by exposing slips of the material during printing, and is known to be complete when the strip shows no colour on being touched with a drop of the developer to be used.

The development is carried out by an alkaline solution of a phenol or an acid solution of an amine (0.25 p.c.). The colours afforded by the various developers are given below :

Alkaline solution of $\beta$ -naphthol	Red.
" " $\beta$ -naphthol - di- sulphonic acid)	Maroon.
" " phenol	Yellow.
" " resorcinol	Orange.
" (slightly) pyrogallol	Brown.
$\alpha$ -Naphthylamine hydrochloride	Purple.
Slightly acid solution of eikonogen	Blue-black.

#### REPRODUCTION OF NATURAL COLOURS.

The problem of reproducing colours as they may be seen on the focussing screen of a photographic camera has long attracted the attention of those engaged in experimental work connected with photography. It is, however, only in recent years that processes founded to a considerable extent on the work of early experimenters have yielded satisfactory results.

This branch of photographic practice has developed so greatly within the last few years that any account of it in a work of this kind must of necessity be brief and somewhat general in its nature, and special works must be consulted for specific details connected with the various processes.

The methods employed for the production of coloured effects on sensitive films may be divided into two large classes. (a) Those where the result is produced by the direct action of light on the sensitive material; and (b) those produced by the intervention of coloured screens, either separate or combined with the sensitive film.

In (a) the colours are reproduced (1) by direct action on the sensitive material, (2) by interference of the waves of light reflected back through the film from a mirror, and (3) by the bleaching out of certain dyes which are responsive to the action of the various coloured rays. In (b) the effects are produced either by coloured screens of various patterns superimposed on the sensitive material or by grains coloured in blue, green, and red, and imbedded in the sensitive film itself.

That a sensitive silver film by itself could respond to coloured rays of light was observed at an early date, and about

1810 the German physicist, Seebeck, showed that different colours produced different effects might be obtained when the solar spectrum was thrown on a film composed of moist silver chloride. Such changes of colour on silver salts were also noticed by John Herschel, Hunt, Fox Talbot, and others; but at that time little progress was made until the experiments of Becquerel and Niepce between 1850 and 1855. In all of them, however, the long exposure necessary to obtain an effect, the very moderate intensity of the colour effect, and the impossibility of permanently fixing the picture, rendered all such attempts impossible for producing results with the camera.

*Lippmann's method by interference waves.* This process, in which no coloured materials or screens are employed, depends upon the production of the colour phenomenon by the interference of light rays reflected from thin films. The plate coated with a transparent emulsion and impregnated with colour sensitising media is placed in a special dark slide with the glass of the coated plate facing towards the lens, and the sensitive film in close juxtaposition to a thin bath of metallic mercury, which acts as a reflecting surface.

The light rays passing through the film are reflected back from the surface of the mercury, thus producing a number of stationary periods or nodes due to the neutralisation of the opposing incident and reflected rays.

The circumstances which produce this effect in the plate may be shown by a diagram (Fig. 8), illustrating the movement of rays of different velocities through a thickness of the sensitive material.

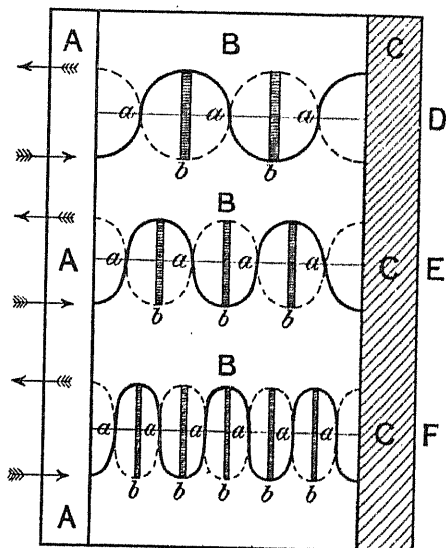


FIG. 8.

In this diagram the rays of the red, green, and blue colours, indicated respectively by the letters D, E, and F, passing through the film and falling on the mercury C, are indicated by the continuous lines, while the dotted lines represent the reflected rays. At the

points *a, a, a*, the rays intersect each other, giving no movement at these points, and, consequently, no light effect, whereas at the points *b, b, b*, or internodal points as they are called, where no interference exists, the action of light will cause a deposition of silver. This deposition taking place at a separation of half a wave length of the incident, light will only reflect light of the colour, the wave length of which is double the distance of these internodal points.

Originally Lippmann employed an albumen process for his sensitive plates, colour-sensitised with erythrosin, quinoline red, cyanine, and malachite green; but more recently formulæ for gelatin emulsion plates have been put forward by Valenta, Lumière, and by Lippmann himself. The following numbers give two forms of the emulsions that have been proposed:—

	I.	II.
A. Gelatin . . . . .	10 grs.	5 grs.
Silver nitrate . . . . .	6 grs.	3 grs.
Water . . . . .	300 c.c.	225 c.c.
B. Gelatin . . . . .	20 grs.	5 grs.
Potassium bromide . . . . .	5 grs.	2.1 grs.
Water . . . . .	300 c.c.	225 c.c.

For colour sensitising cyanine and erythrosin solutions (1:500) have been used. For the sensitiser 2 parts of the cyanine solution is mixed with 1 part of the erythrosin solution, and 1 to 2 parts of this mixture added to 100 parts of the emulsion. Increased sensitiveness may be given by the addition of silver nitrate shortly before use. To which 5 c.c. of acetic acid have been added.

*Ives' process.* This process, devised by Ives in America and by Ducos du Hauron in France, depends on the principle put forward by Clerk Maxwell, that the object to be reproduced, if photographed through three differently coloured screens, will give a representation representing in light and shade the gradation to which the different light effects coming from the object will excite a single primary colour sensation in the eye. Three negatives of the object are obtained, one taken behind an orange screen, a second behind a green, and a third behind a blue screen. Three positives are then taken from these negatives, and are illuminated one by red, the second by green, and the third by blue violet light. These being superimposed on a screen, the combined image of the original object will be seen reproduced in its natural colours.

For the simultaneous production of the negatives and for the projection on the screen, special cameras have been devised, and for viewing the transparencies Ives introduced the apparatus known under the name of the 'Kromoscope.'

The same effect may be obtained on one glass plate in the following way. Three separate negatives are taken, paying due attention to the exposures necessary for the different coloured filters. These are developed in the usual way, fixed and washed. To obtain positives from these negatives, an ordinary transparency is first taken from the negative obtained through the red screen, washed and dried. It is then bleached by immersion for about a minute in a

solution of potassium ferricyanide, washed with water, and placed for a minute and a half in the red staining solution. The stained film is then transferred to a solution of sodium thiosulphate, which at first causes a brown precipitate. This is at once thrown off and fresh thiosulphate flowed over the plate, when the image will gradually assume a greenish-blue colour. The plate is now washed, dried, varnished with a celluloid enamel, and again dried.

The pink and yellow images may then be printed at the same time on one strip of a sensitised dichromated gelatin film, the celluloid side of the film, not the dichromated side, being in contact with the film side of the negative, so that the print is made through the celluloid support. The film is then developed in the usual manner by hot water at a temperature of 95°–100°F., fixed by sodium thio-sulphate, and thoroughly washed with cold water. The two prints are now cut separate and stained by the pink and the yellow dyes. The staining should be carried out in white porcelain dishes, and should be done slowly.

When the stained transfers have been rinsed and dried they are ready to be superimposed in correct position over the blue transparency first described. The pink film is first accurately adjusted film to film over the blue, and then the yellow, stained side downwards, over the pink. The films may be fixed in accurate register with binding slips, but a better result is obtained if the separate films are secured in optical contact by Canada balsam. When thrown on the screen the original picture is reproduced.

*Dyes for tri-colour staining.* The following are some of the substances which may be used. For blue: thio blue A or soluble Prussian blue, slightly acidified with sulphuric acid. For pink: a mixture of eosin and rhodamin pink. For yellow: best brilliant yellow or aniline yellow. For Ives' plates. For blue: methylene blue, 10 grs.; cold water, 4 oz. For pink: magenta red, 16 grs.; hot water, 4 oz.; acetic acid, 10 mins. For yellow, ammonium picrate, a saturated solution. In each case the transfer, after staining, should be rinsed in water slightly acidified with acetic acid.

The nature of these dyes is very varied, and special works must be consulted with regard to quantities and methods of preparation.

*Light filters for colour work.* These may be made with either a collodion or a gelatin medium coated on glass or used in cells. For yellow light filters: tetrazine, rapid filter yellow K; aurantia, and naphthol yellow may be used. For orange filter a mixture of aurantia or rose Bengal with tetrazine is employed.

*Filters for three-colour work.* For these a 6 p.c. stock gelatin solution is the medium. For the violet filter (yellow printing negative), stock dye solution, crystal violet, 31 grs.; warm water, 6 oz., 76 mm.; glacial acetic acid 3 mm. Add 20 parts dye solution to 100 parts gelatin solution. A second blue dye is rapid filter blue, 15½ grs.; water, 6 oz., 160 mm.; ammonia, 10 mm. Filter, then take dye solution 20 parts; gelatin, 100 parts. For green filter (red printing negative). Rapid filter green I., 62 grains; water 3½ oz. Take of dye solution 20 parts to 100 of gelatin solution. A green for



panchromatic plates is as follows: filter blue-green,  $15\frac{1}{2}$  grs.; filter yellow K,  $15\frac{1}{2}$  grs.; water  $3\frac{1}{2}$  oz.; take dye solution, 20 parts; gelatin, 100 parts. Red filter (blue printing negative). Rapid filter red 1.,  $38\frac{1}{2}$  grs.; water,  $3\frac{1}{2}$  oz. Take dye solution 20 parts, gelatin 100 parts.

*Single plate coloured processes. Joly's process.*

In this process a glass screen, which may be called for convenience the taking screen, is ruled mechanically with minute lines in orange, yellowish-green, and blue. This screen is placed in the ordinary camera slide with the lined surface inwards and in contact with the film of the sensitive plate. These plates must be sensitive to the entire range of colours. The negative having been developed in the usual way a positive is printed from it by contact, and another ruled screen is placed in contact with this transparency. This second screen, which may be called the viewing screen, is not lined like the first one, but in red, green, and violet lines. This screen must be so adjusted that the red lines fall on the orange line occupied by the orange line screen; the green on that blue-green, and the violet on that occupied by the blue. It is of importance that the lines be in exact register. The positive and screen having now been put in exact position, the image can be thrown upon a screen, when the picture will be seen in its original colours. It is of advantage that these pictures should be looked at from some little distance, as the lines blend more harmoniously, and they should also be looked at directly, as when seen obliquely the colours vary. When observed directly the lines on the positive, and those on the viewing screen are in register; but when observed obliquely, the blue or red predominate, according to the side from which the transparency may be regarded.

*Autochrome process.* In this process, introduced by Lumière, the colour screen consists of minute starch granules dyed with the three primary colours, red, blue, and green, this film being overlaid by a panchromatic sensitive film. In preparing these the plates are first coated with a tacky film which is then covered with a layer of the coloured granules thoroughly mixed, so that the different colours may be as far as possible uniformly distributed over the plate. This film is then rolled so as to get it as thin as possible, and retaining on its surface only one single thickness of the coloured particles. It is then dusted with some black material to fill up the interstices between the coloured granules, and finally dried and varnished. In some cases the dark material is incorporated in the emulsion containing the coloured granules. Upon the plate so prepared is spread the panchromatic sensitive emulsion, which is dried in the usual manner and it is then ready for use.

The plate, as in the case of all such in which the coloured screen is attached to the sensitive film, must be exposed with the glass and not the emulsion towards the lens, so that the light coming to the sensitive film must pass through the coloured filter. The lens must also be covered with a yellow screen to diminish the active effect of the violet-blue rays.

This reversal of the position of the plate in

the camera necessitates some adjustment of the focus in using an ordinary carrier and ground glass focussing screen. Such compensation can be made either by reversing the ground-glass screen or by racking in the lens about  $\frac{1}{10}$  of an inch towards the plate, thus compensating for the depth of the glass plate on which the emulsion is spread. It may also be arranged for in more simple manner by focussing the image on the ground glass before placing the yellow screen in its position behind the lens. On screwing the yellow screen into its proper position, after focussing in the ordinary way on the screen, the image will be found perfectly sharply reproduced on the developed plate after exposure.

*Dufay's dioptrichrome process plate.* In this the colour screen consists of a series of parallel green lines with the intervening spaces filled by alternate blue and red squares. The breadth of the lines and the size of the squares have a certain relation; thus the width of the green line is 0.06 mm.; the blue square is 0.06 mm., and the red square 0.07 mm. The plates are rapid and are said to be stronger for handling than some of the others.

*Thames screen plate.* This plate has a colour screen formed of rows of alternate red and green circular disks, the intervening spaces being filled with a violet-blue dye, thus covering the entire plate with the three colours. The Thames plate can also be obtained with the colour screen separate from the sensitive plate.

In these plates the screens are apparently more transparent than when coloured granules are used; also they can be exposed with a lighter yellow screen upon the lens and probably are more rapid in their action.

*Development of coloured positives.* Unless it be necessary that the resulting positive should undergo intensification, the development may be carried out with only two solutions, the developer and the reversing solution. The same reducing agents, with some slight modifications, may be used in the ordinary development already described. The most important differences from the ordinary manipulation in the development of coloured positives are that the light of the developing room must be much more modified on account of the sensitive nature of the plates, and the washing operations as short as possible on account of the delicate nature of the films.

The first development is carried out in the usual way, but should be finished in 2 to 2½ minutes; the plate is then carefully washed and covered with the reversing solution. The action of potassium metabisulphite is examined. At this stage the plate should be examined.

in the reversing solution for 3 to 4 minutes, but must be closely watched. It is then again washed and flooded with the same developer as employed in the first development. Both the reversal and the second development may be carried out in daylight and the action of the second development allowed to proceed until the positive becomes uniformly dark or nearly black when viewed in the dish by reflected light. Should the positive appear dull or slightly stained after reversal it may be cleaned by immersion in a 1 p.c. solution of sodium

Full instructions are generally given on the various plates. They may be taken as more or less applicable to plates where the colour screen is combined with the emulsion.

#### Developers.

	<i>a</i>	<i>b1</i>
Metaquinone	$\frac{1}{2}$ oz.	—
Sodium	$3\frac{1}{2}$ oz.	—
Potassium bromide	90 grs.	60 grs.
Ammonia (0-920)	9 drs.	—
Hydroquinone	—	$\frac{1}{2}$ oz.
Potassium metabisulphite	—	$\frac{1}{2}$ oz.
Water	35 oz.	20 oz.
Caustic potash	—	1 oz.
Water	—	20 oz.

*a* is the developer generally applicable to autochrome plates and *b1* and *b2* to Thames plates. In these latter, *b1* and *b2* should be mixed in equal quantities just before use.

#### Reversal.

	<i>c</i>	<i>d</i>	<i>e</i>
Potassium permanganate	30 grs.	—	—
" dichromate	—	45 grs.	10 p.c. solution 1 oz.
Sulphuric acid	35 drs.	100 mm.	1 dr.
Water	35 oz.	20 oz.	10 oz.

*c* and *d* are useful for autochromes, *e* is generally used with the developers *b1* and *b2* for Thames plates. In using potassium permanganate as the reversing agent it is often necessary to immerse the plate for a few seconds in a bath of chrome alum immediately after reversal and before the final washing.

**Intensification.** Should the plate after development appear to want contrast and brilliancy it may be intensified either at the time of development or at some future time provided it has not been varnished. Before intensification if the plate has been allowed to dry a thin edging of varnish should be given to it to prevent the film frilling or slipping.

The plate is first immersed for about 15 seconds in a solution of—

Acid permanganate from developer (*c*) 5 drms.  
Water . . . . . 35 oz.

After washing it is intensified much in the same manner as described for wet plate positives in the following solutions:—

I.	{ Pyrogallol . . . . . 45 grs.
	{ Citric acid . . . . . 45 grs.
	{ Water . . . . . 35 oz.
II.	{ Silver nitrate . . . . . 75 grs.
	{ Water . . . . . $3\frac{1}{2}$ oz.

Of these for any size up to a whole plate take of I.  $3\frac{1}{2}$  oz. and of II. 3 drms.

Immerse the plate in this solution and examine the increase in intensity from time to time. The solution must be made just before use and discarded when it becomes turbid. After intensification, gently wash the plate for a few seconds and immerse in a bath of neutral permanganate containing potassium permanganate 15 grs. to water 35 oz. Wash again for a few seconds and fix the plate in the following bath: sodium thiosulphate,  $5\frac{1}{2}$  oz.; saturated solution of sodium bi-

sulphite,  $1\frac{1}{2}$  oz.; water, 35 oz. The plate after a final washing can then be dried. Fixing the plate is always necessary after

**Bleaching-out process.** This process depends upon the fact that certain dyes may be destroyed by the rays of light which they absorb. Thus an unstable red colour will be stable in red light but be destroyed by light of another colour; this phenomenon, as explained by Herschel, being due to the fact that only those rays which are absorbed by a dye can exercise their energy in decomposing that dye, the other rays which are reflected having no action upon it. Thus if a film be constituted of properly chosen yellow, red, and blue dyes, only those dyes will be destroyed which absorb the rays of the corresponding colour. If paper be coated or otherwise with sensitive aniline colours which are susceptible to this decomposition and a coloured transparency be placed upon it, wherever green light falls upon the paper the red and blue colours will bleach out, and conversely where red falls the blue and green will bleach, and where blue rays fall the red and green will go. In fact, wherever a particular colour falls, that special colour will be retained and rendered permanent on the paper print.

The following quantities have been given as suitable for preparing a sensitive film for this process:—

A.	Gelatin . . . . . 154 grs.
	Distilled water . . . . . $3\frac{1}{2}$ oz.
(1)	Methylene blue . . . . . $\frac{1}{2}$ grs.
	Distilled water . . . . . $\frac{1}{2}$ oz.
(2)	Auramine . . . . . $\frac{1}{2}$ grs.
	Alcohol . . . . . $\frac{1}{2}$ oz.
(3)	Erythrosin . . . . . 4 grs.
	Distilled water . . . . . $\frac{1}{2}$ oz.

To the gelatin solution A add of No. 1 solution 68 min., and of No. 2, 34 min., stir well and then add drop by drop with constant stirring 25 min. of No. 3 solution. The addition of No. 3 must be stopped on the slightest appearance of a red tinge. The mixture should stand for 3 or 4 hours at a temperature of from 95° to 110°F., and then should be added a solution of chloral hydrate 31 grs. and caustic soda solution 30 p.c., about 10 min.

The length of exposure necessary to give any good result is at present so long, that this method of obtaining coloured prints cannot be said to be quite perfect enough for ordinary use. Improvements, however, are being made. It will be seen that this process, if the films be spread on paper, might be used for printing from coloured transparencies.

#### PRINTING IN COLOURS ON PAPER.

In the processes hitherto described the result obtained is a coloured transparency on glass of which only one copy can be retained. To obtain a number of copies on paper, resort must be had to photo-mechanical work. The principles involved in these processes will be dealt with elsewhere (p. 236), so that here it is only necessary to describe the differences which exist when producing such pictures from coloured transparencies.

Three negatives of the subject are first taken through proper colour filters as already described,

and from these, corresponding positives are made on ordinary sensitised plates. Cross-hatched negatives are now made from these positives through lined or dotted screens as for ordinary photo-mechanical printing, which negatives can be printed on copper or zinc plates coated with dichromated gelatin. Development by washing is then carried out in the usual way, leaving a positive in insoluble gelatin on the copper or zinc plate. These constitute the three blocks, as they are called, and may now be coloured separately in yellow, red, and blue, the final prints being taken from them by carefully superimposing and adjusting the sheet on which the final impression is to be taken. The order in which the final printing is carried out is first to print the yellow image then the red and finally the blue.

*ColloTYPE colour process.* The final prints in this process are obtained in the various colours from a reticulated gelatin surface. Three negatives are taken in the manner already described on thick glass plates covered with dichromated gelatin, and after exposure washed to remove the colour of the dichromate. When dry the plates are soaked in glycerol and water for about 30 minutes, and the solution carefully removed by a dry cloth. The glycerol solution penetrates through the film, apparently according to the different intensity of the light that has acted on various parts of the plate. Thus there is great penetration in the parts unacted on by the light, but little or none on the portions hardened by the light. On covering the surface with coloured ink, the greasy body adheres to the dryer shadows, but does not become attached to the more moist portions which represent the high lights. The final impressions are taken by accurately superimposing the sheet of paper successively over the three differently coloured colotype plates. The reticulation of the gelatin in this process provides the necessary fine grain on the plate.

*Inhibition process of Sanger-Shepherd.* Three negatives are first taken through the colour screens, and positives printed from them on a celluloid film coated with gelatin containing silver bromide, which is sensitised in a solution of potassium dichromate. The prints are made by printing through the celluloid film, the celluloid surface being in contact with the film side of the negative. Exposure is carried on until all details are visible on the film as a dark yellow print. The film is now washed for some minutes in water and then fixed with sodium cyanide, leaving all the white silver bromide unacted on, leaving the image in clear gelatin. The film, taken under the green filter negative, is now stained in the pink dye bath, that from the blue filter in the yellow dye bath, and the third stained in the blue dye.

The prints are then successively 'squeezed' on to a sheet of paper which has been coated with a thin layer of gelatin, and which after well soaking in water is spread on a glass plate. The order in which the dyed positives are transferred to this coated paper is, first the one dyed in the pink colour, second the yellow dyed positive, and finally the one with the blue dye. By this means a combined print formed from the three combined colours is obtained.

*Pinatype process.* This process depends

upon the use of certain dyes which do not attach themselves to the hardened gelatin, but are capable of staining the unacted on gelatin. This is the reverse of the last described process, and as the dyes do not attach themselves to the hard, but only to the soft gelatin, the print in this case will be a facsimile of the original negative. In order, therefore, to make a positive print, the dichromated plate must be made from a transparency and not from a negative.

Three negatives having been taken through coloured screens, three positives are copied from them on an ordinary emulsion, similar to that used for lantern slides. From these positives, three sensitised dichromated printing plates are made, which after washing and allowing to dry are dyed with blue, red, and green pinatype dyes; a blue bath for the plate made from the red screen negative, a red bath for the plate from the green screen negative, and a yellow bath for the third plate.

To print the picture on the transfer paper, which has been previously well soaked in water, it is gently pressed first on to the blue dyed plate, then on to the red and finally on to the yellow. It is not absolutely necessary to follow this order, as it has been found advantageous to alter it for different subjects. About 10 minutes will suffice for the transfer of each colour to the transfer paper, but for details with regard to this and for the minute manipulation of the process, special instructions must be consulted. It will be observed that a certain advantage exists in this process, as the three colour im-

pressions are on the one gelatin support. A process employing only two colours has been introduced by Gurtner of Berne. In this process, one of the blue and yellow transparencies is paid to the red. The transparency plate is first dyed in the dark for a few minutes in an aqueous solution of naphthol orange and then dried. This plate is now placed film to film in contact with an ordinary panchromatic plate in the dark slide, so that the glass of the former, or transparency plate, faces the lens. With this arrangement the orange dyed plate acts not only as the sensitive plate for the blue rays, but also as a light filter for the red, yellow, and green rays. In this way, the transparency plate becomes the negative for the yellow print, and the panchromatic plate that for the blue print.

From the transparency plate the red print is made by placing it on a sheet of paper or some other support. The transparency or yellow plate, after fixing and washing away the stain, may be printed from on ordinary printing out paper, or on a stripping collodion-chloride paper, and if the prints be fixed with ammonia without toning they will retain a proper yellow-red tone. If transparencies are used the yellow transparency is directly combined with the blue by placing the plates film to film. If prints on paper are required, then the print on the stripping collodion-chloride film after careful adjustment is superimposed on the blue print.

J. M. T.

#### PHOTO-MECHANICAL PROCESSES.

In addition to the processes of pure photography in which the results are obtained by

light action aided by subsequent chemical operations, there are other methods of photographic picture making. These constitute a group by themselves of considerable industrial importance, differing from the purely photographic methods in so far that they yield their results partly by chemical and partly by mechanical means. Photography is utilised in the production of surfaces from which prints are afterwards obtained in printer's ink. Such processes employ the different forms of printing press, and, to them the term *photo-mechanical* is applied. They are used for the production of transcripts of drawings and paintings of different kinds and for the multiplication of copies of photographs of natural objects. By far the greater portion of the illustrated books and periodicals now made utilise photography in this manner. The processes are divided into three groups, *intaglio*, *surface*, and *relief*, according to the form of the ink-bearing medium. The term 'surface' is for convenience generally employed (although it is not strictly correct), and it is the function of this *photo-mechanical* prepared surface to hold the ink which is to be transferred to paper (distributed in such order and quantity as will render the various tones of the picture. For a simple understanding of the differences in the three groups, consider a plane surface as the starting-point. Then, in an *intaglio* process, the ink-holding portions are sunk below that surface, as, for example, in a steel engraving—in a *surface* process the ink-bearing parts and those which do not bear ink are in the plane of that surface after the manner of a picture upon a 'lithographic' stone, whilst in a *relief* process certain portions of the original surface have been removed, forming depressions, leaving other portions which are to bear ink standing in relief, the simplest illustration of this form of surface being an ordinary woodcut. It will be seen that a relief process—so far as the finished result is concerned—is the exact reverse of an *intaglio* process. Methods coming under these two designations yield printing results which fulfil their purposes by utilising purely mechanical principles. This is not so, however, with surface processes, for the physical state of the surface produced by chemical change largely determines their working.

The following list gives the typical and more important processes according to their character in the groups already given:—

#### *Intaglio.*

- Photogravure in line and in gradated tones  
—flat surface.
- Photogravure in line and in gradated tones  
—cylindrical surface.
- Woodburytype.

#### *Surface.*

- Photo-lithography.
- Photo-zincography.
- Alagrophy.
- Collootype.

#### *Relief.*

- Line block processes.
- Tone " "
- Colour processes (tri- and multi-colour methods).

Combination processes between methods in the same group or between those in more than one group, as for example, collotype and lithography, lithography and tone block processes, lithography and photogravure.

Negatives required for photo-mechanical methods are made by means of wet collodion, collodion emulsion, and by dry plates. The first-named process is the one principally used for the majority of cases, for the reason that it is the most rapid and gives easily the kind of negative required. When, however, subjects in colour are to be rendered either in monochrome or again in colour, the choice lies between the two latter methods. The modern orthochromatic dry plate of the best type has, however, very largely replaced collodion emulsion and will probably in time do so entirely.

The second step is the making of the surface. Practically the whole of the photo-mechanical processes are based upon the action which occurs when albumen, gelatin, or other collodion product gelatose (of which the substance 'fish glue' is the most important example), are exposed to light in conjunction with alkali dichromates. Generally the insoluble bodies so produced are employed as protective agents or 'resists' upon the surface of a metal against the action of some solvent of that metal (photogravure and relief processes), or they may be used in the production of an image to be applied to stone or metal as an intermediary (lithography, zincography, alagrophy), or to paper as finality (collootype).

#### *Intaglio Processes.*

*Woodburytype.* This process was the invention of the late W. B. Woodbury, and is especially interesting in that it forms a bridge between the purely photographic and the photo-mechanical process. The printing plate consists of a sheet of lead which is impressed with a series of cavities the variation in depth of which corresponds to the light and shade of the different portions of the picture it represents. A carbon print (see *Chromium Printing*, p. 241) is a picture produced in insoluble gelatin which holds in suspension finely-divided carbon or other pigmentary matter. The picture tones are represented by various thicknesses of insoluble gelatin, and such tones show a sensible amount of relief. By the use of a specially thick film of gelatin the amount of relief may be increased, and if such a film be developed upon a film of collodion there is obtained what is known as the Woodbury 'relief,' which is merely a carbon picture held upon a thin film of textureless collodion instead of upon the fibrous paper, as is customary with a carbon print. When the film is dry, there are varying thicknesses of hard gelatin, and it so happens that such is capable of resisting considerable pressure. If the relief be laid upon the bed of a hydraulic press and a sheet of pure lead be put above it and pressure applied (the precaution being taken to prevent the lead flowing laterally), a perfect mould will be made of the relief, and without damage to the gelatin picture. The gelatin relief can be readily removed and the result will be an *intaglio* copy in lead. If,

when the carbon print has been removed, the space left is filled up with a solution of gelatin containing pigment and this gelatin is allowed to set, to all intents and purposes, the condition is the same as it was in the first instance, except that one filling material was dry gelatin, and the other is wet gelatin. If we allow this gelatin to set, attaching to it previously some substance by which it can eventually be withdrawn, a print will be produced similar to the one used for making the mould. The latter was a carbon print produced by the agency of light, and now from a leaden intaglio plate or mould a similar carbon print is obtained, purely by mechanical means and without light action. When once the leaden relief is produced, prints are readily made merely by pouring into the mould a solution of gelatin containing pigment suitably adjusted as to quantity, placing on the top a sheet of paper, and applying even pressure above. The excess of gelatin is squeezed out at once, that remaining in the mould sets in a short time, and upon lifting the paper away the gelatin will come with it. A Woodbury print is then simply a carbon print produced mechanically and consists, as does the carbon print, of a layer of gelatin of varying thickness, the only other difference being that in the case of the light-produced carbon picture the gelatin is insoluble, and in the mechanically-produced carbon print it is not. This process is probably the most perfect of all the photo-mechanical processes, so far as the rendering of tone is concerned. Very great variety can be obtained, the colour depending upon the pigment used with the gelatin. The process *Stunnotype*, also due to Woodbury, was a modification of this method designed to avoid the necessity for hydraulic pressure in the production of a mould. The plate was formed from a negative carbon relief in gelatin faced with tin foil forced into contact with the relief by rubber roller pressure.

**Photogravure.** A photogravure plate is a sheet of copper bearing an image formed by means of cavities of different depths, which represent the gradations of the picture. These cavities are filled with an ink composed of linseed varnish and a pigment (for example, lamp black), which ink is afterwards transferred to paper by means of pressure in the copper plate printing press. The process most generally used is that known as the Talbot-Klic.

Any drawing in line or graduated tones in monochrome or colour or any photograph of a natural object may be rendered by this process. Whatever be the original, a negative must first be prepared of the desired size, and from this negative a positive transparency is made which should be laterally reversed. If the subject be a line drawing the positive may be produced by means of a gelatino-bromide dry plate or by wet collodion. If the negative represents a drawing in graduated tones—for example, a wash drawing, an ordinary water colour or a photograph of a natural object—the negative must be unreversed and from it a positive transparency is made by the carbon process, which produces the reversal required without further operation. The method gives probably the best rendering of tone, but in the hands of a skillful operator a reversed positive may be made by the dry-plate process. The latter plan has the advantage

that the size of the positive may be varied from that of the original negative which is frequently required.

**Outline of process.** The process of photogravure consists in forming upon the surface of a sheet of copper, on which there is deposited a fine dust of bitumen (or colophony), an insoluble gelatin image. The plate bearing the dry gelatin image is placed in a solution of ferric chloride which is absorbed, when swelling and penetration of the film takes place—the solution eventually reaches and then etches the metal. This process may be termed 'through' etching. The various thicknesses of the gelatin which form the gradations of the image determine the amount of etching produced by the action of the mordant, so that in a given time different amounts of etching are produced, corresponding to the tones of the picture. When the etching is completed the gelatin is removed, the plate cleaned, and it is then ready for proofing in the press.

This gelatin image governing the etching is a negative image, and is the 'resist.' It is produced by the carbon process, in the ordinary manner of the carbon printer, by developing on the metal a tissue exposed under the reversed positive from the negative of the subject. The dust coating is termed the 'grain.' Its function is to protect minute areas of the surface of the metal from the attack of the mordant. A patch of uniform tone of appreciable size is not represented by an etched cavity corresponding in area to that patch of tone, but is made up of a number of small ones, undistinguishable as separate elements by the unaided eye.

Failing this condition—however it may be produced—in the plate, the printing ink could not be held prior to transfer to the paper which forms the final support of the image.

The 'grain' is produced by exposing the plate in a box which contains suspended in its atmosphere very finely divided bitumen or colophony. The 'graining box' must be of considerable volume and large in horizontal sectional dimensions in proportion to the dimensions of the copper plate, in order to enable uniform graining to be obtained over the whole area of the surface. When the amount of dust deposited is sufficient the plate is removed and gently heated, when the grains soften and adhere firmly to the metal. The success of the process is largely dependent upon suitable graining of the plate.

The copper used for plate making must be pure, hard, and homogeneous; the surface planished and highly polished. The carbon tissue is preferably one containing only a small quantity of pigment in order that the colour of the metal may be seen through the film. The correct exposure for the tissue under the positive should be ascertained by trial exposure, developing such trials upon opal glass.

The solution of ferric chloride (which must not contain any free acid) is employed as mordant in a solution of 10% salt in water to which is added a few drops of sulphuric acid which registers 45° Baume at 16°C., and from this solution others are prepared by dilution to densities 33°, 35°, 38°, 40° and 43°B. The more concentrated the mordant the slower the rate of penetration. A very concentrated solution may not in reasonable time penetrate even

the thinnest portion of the resist. If such fails, the solution is poured away and a weaker one employed. When the ferric chloride reaches the copper, a darkening takes place showing that the etching has started. Such action will continue to other and lighter tones as the mordant penetrates, and to secure this end the weaker solutions are used successively until even the thickest layer of gelatine is penetrated. Errors in timing or in the use of unsuitable solution lead to faulty rendering of the scale of gradation.

When the etching is completed the metal plate is at once placed in a solution of caustic soda, which arrests the action of the mordant. The plate is washed in water, scrubbed with a soft brush, brushed with dilute sulphuric acid, and afterwards with turpentine to remove the "grain," again washed and dried.

The plate is printed after the manner of a copper plate etching, and in photogravure much of the success is due to skillful treatment in this operation. If only a few copies are required the plate may be printed at once; but for any quantity it is necessary that the surface be 'steel faced,' in order to protect the image from wear in the printing process.

Usually photogravure plates require considerable modification in the hands of a skillful engraver by means of the burnisher and roulette, and by a process of selective etching for which the plate is afterwards specially prepared.

#### INVERT HALF-TONE INTAGLIO PRINTING.

A form of intaglio printing consists in adapting the ruled screen half-tone principle (see *Tone block processes*). A screen positive is made from an ordinary negative (continuous tone) and from this positive a print is made upon copper by the enamel process (see *Enamel printing*). This print forms the resist. The plate is afterwards etched in a solution of ferric chloride, and the etched metal is printed in the copper plate printing press. The gradations of light and shade are rendered by dots of various sizes (the number per unit area depending on the ruling of the screen employed when making the screen positive), as in the half-tone block process, but each etched cavity is the same depth.

#### ROTARY PRINTING OF INVERT HALF TONE.

Instead of using a flat surface of copper, a cylinder of the metal may be employed. This offers considerable advantages, inasmuch as it permits of the rotary method of printing with the consequent gain in speed of output and in certain other directions the process is useful, as, for example, in the illustration of the less expensive forms of printed matter, newspapers, periodicals and the like. Special devices are used by which the sensitive coating (fish glue and an alkali dichromate) is applied to the roller and a flexible film form of half-tone screen positive is caused to adhere to the cylinder by a suitable fluid medium—as, for example, mineral oil—which does not affect the sensitive coating. After exposure to light, the image is developed, dried, and enamelled. Those portions of the roller not covered with an image are now varnished by a protecting medium

and afterwards the roller is treated with the mordant. The printing of such cylinders differs from that employed with any other photo-mechanical process. The machine employed consists of a large cylinder or bowl upon which is stretched a felt blanket, and over this is fed the paper from an endless reel. The engraved roller is supported in contact with the printing paper, the pressure between the two being variable at will. The inking is effected by supplying the printing colour to the roller as it revolves by the aid of a brush or felt feeder. The excess of colour is removed by means of a thin steel knife-edge blade termed the 'doctor,' which is caused to press upon the roller with sufficient pressure to remove the superfluous ink from the surface. The colour remains in the etched hollows. The surface-clean portion of the roller next comes in contact with the printing paper, when transference of the colour from the cavities takes place. It will be seen that the steel 'doctor,' with its perfectly smooth edge replaces the hand wiping of the copper plate printer. Perfect fitting of the two surfaces, the 'doctor' and the cylinder, is necessary. The ink used must be much thinner in consistency and of a different character to that employed for ordinary copper plate printing or the surface of the roller cannot be made clean by the 'doctor.' This method of inking does not offer the same opportunity for modification as that used by the ordinary copper plate printer, whose craft is extremely personal, offering abundant field for the exercise of taste. In consequence, excellence of result in all 'doctor' or mechanically wiped intaglio printing depends largely upon the quality of the engraving work.

#### ROTARY PRINTING OF PHOTOGRAVURE.

*Rotary photogravure.* The method of printing ordinary photogravure plates does not lend itself to speed of production, and the result is that the prints are relatively costly, especially for large sizes. Photogravure plates, as in the case of ordinary copper or steel intaglio etchings, can be printed with success upon special flat-bed printing machines, when the wiping of the plates is effected by means of a 'doctor' or by a travelling band of paper. It is, however, found in the case of the delicate photogravure plate that considerable wear takes place. For some years, the rotary principle has been applied with great success in the case of a limited number of firms, where methods of producing the etched rollers are carefully guarded secrets. The 'invert half tone' process should not be regarded as the same as photogravure, for the reason that 'through etching' is necessary to give the characteristic effect of the latter process, the etched cavities of the rotary photogravure plate, unlike 'inverted half tone,' varying in depth, an important element in producing the beautiful effects of the method. If upon the surface of a copper cylinder there be developed a carbon print made by exposing a sheet of sensitive dichromated tissue under a ruled screen (see *Half-tone process*) of special type (Fig. 12), the tints so produced—which are formed of regularly distributed elements of insoluble gelatin—may be utilised in place of the bitumen grain employed in the Talbot-Klic

process. Upon this ground, a carbon negative image—as in the Talbot-Klic process—is developed and the roller with duplex resist is, when dry, submitted to the action of ferric chloride. The roller so prepared is then printed after the manner previously outlined.

The quality of result obtained by the rotary process adopted by the best firms is very high, the rollers being singularly free from obvious evidences of the use of the hand engravers' tools. This is largely due to the perfection of the method itself and to the attention paid to the making of the negative and positive and to their skilled retouching. The printing ink—the medium, pigment, and viscosity—the paper used, and the speed of printing require very careful adjustment, the one to the other, and to the particular engraving on the roller.

*Photogravure in colour.* Prints in colours are produced by applying colour inks to the engraved plates, which are etched more deeply than for monochrome. The coloured inks are applied to the plates by sponges or by dabbers of different sizes and for small details by stumps, and the plates are wiped by the usual muslin and also by the soft portion of the printer's hand. The transfer of the ink to the paper is completed at one operation. The process is naturally slow, and the results, though often very fine, are costly.

Recently, the process has been applied to the production of photogravure prints in colours with success. Combinations of rotary photogravure and lithography for colouring work are also employed.

#### CHROMIUM PRINTING.

If gelatin be placed in a cold solution of an alkali dichromate, the body swells, behaving in the same manner as when immersed in water. If the swollen mass be dried and kept in the dark without special precaution, no alteration takes place which materially affects the properties of the gelatin except after some hours. The period of immunity from change largely depends upon the temperature and the amount of moisture present in the mass. In warm and especially during damp weather, a material change may take place in 12 hours, and the result of that change is that the gelatin has reduced some of the chromium salt, the mass has lost its yellow colour becoming dull orange, its absorption capacity for water, and the increase in volume consequent, is lowered, and the temperature at which the body when swollen in water passes from the 'gel' to the liquid state is raised. As time goes on, the changes in the normally dry chromated mass increases, with the result that the gelatin almost wholly refuses to absorb water, and it will not dissolve at increased temperature—the gelatin has become insoluble.

If the dichromated gelatin be kept in a cool and dry atmosphere it will remain practically in its original state for several days; and with complete desiccation, no change of moment can be observed after many weeks' storage.

The change in appearance and behaviour thus indicated proceeds with great rapidity in the presence of light, provided that the di-

chromated gelatin is ordinarily dry. In the moist state the alteration is extremely slow. Gelatin may therefore be said to form in conjunction with a dichromate a mixture sensitive to light. What is true of gelatin holds good for many other substances: for example, to its parent *collagen* and to its primary degradation product *gelatose*, to albumen, gum arabic, and to starch. All these substances reduce alkali dichromates in the dark, but more rapidly in the presence of light, and yield residues which are insoluble in hot water. Many bodies akin to those instanced—gelatin peptone is important in this respect—reduce dichromates but do not yield insoluble products. The feature which it is important to notice is the change in solubility in water and the properties which accompany this change, for upon these the interest and value to the photographer and to the photo-mechanical worker depend.

Insolubility finds its most important application in the 'carbon' or 'autotype' process, which is one of the most perfect printing methods employed by the photo-mechanical worker. Both on account of the faithful reproduction of the gradations in the negative and the effect which may be produced. In order to obtain pictures by this process, a sheet of paper coated with dichromated gelatin containing in suspension a suitable pigment, is exposed under the negative. The gelatin becomes changed according to the degree of exposure to light, which is determined by the opacities of the different parts of the negative, and such changed gelatin is insoluble in water. If after exposure the sheet be treated with hot water, the unchanged gelatin is removed and the insoluble portions remain. Inasmuch as the insoluble gelatin remaining upon the paper contains uniformly suspended pigment, it follows that the picture tones will be formed by varying amounts of such pigment, the gelatin acting now as the vehicle. The term 'carbon printing' had its origin in the fact that lampblack was used as the pigment, and this body is still employed in many forms of the sensitive paper or 'tissue.'

The sensitive tissue prepared for the process, is made by coating the surface of suitable paper with a mixture of gelatin, sugar, and colouring matter in water to which an alkali dichromate is added. The machinery employed for the purpose is simple in character, the paper being merely drawn across the surface of the mixture, which is kept liquid by heat, the speed of travel with any preparation determining the thickness of coating. The paper is afterwards suspended in a room through which a current of air is passing. After drying, the tissue is sensitive to light. If the dichromate be omitted, insensitive tissue results. Both forms are manufactured in large quantities. Tissue is produced in a large variety of colours, and care is taken by the makers to use only pigments or mixtures of pigments which are permanent in light. When such rule is followed, carbon prints are perfectly permanent. The insensitive tissue may be sensitised by immersion in an aqueous solution of potassium dichromate after which operation it is dried. The concentration of such solution, which varies between 1 and 5 p.c., exercises a marked influence on the character of

the print, the contrast decreasing as the amount of dichromate is increased.

When the sheet of sensitive tissue is exposed under a negative, all portions of the surface of the tissue, except those under absolutely opaque parts of the negative, are changed, and there is formed therefore a skin which is insoluble in water. Such skin acts as a protective coating against the action of the warm water used in removing the soluble portions in development. If such an exposed print be placed in warm water the soluble layer remaining under the

the insoluble part . . . . . hold the paper and no picture is produced. How to meet this difficulty was one of the problems in the early stages of the development of the process. Such difficulty is now avoided in a simple manner. If the exposed sheet be placed in cold water together with a sheet of glass and the gelatin surface (which was in contact with the negative) is fixed upon the glass and the two are afterwards pressed together by means of a squeegee so as to exclude all air, the gelatin paper will, after standing, adhere tenaciously. If the tissue so mounted be now placed in hot water, the paper can be stripped away and will leave the gelatin mass adhering. By gently laving the soluble gelatin washes away, leaving the insoluble gelatin behind. This picture forms a transparency, and such are of considerable value for the various purposes for which positive pictures upon a transparent base are required. If instead of using plain clean glass a sheet which has been polished with a cloth moistened with a turpentine solution of resin and beeswax is employed, the dried picture may afterwards be transferred to paper by the simple expedient of pressing into contact a sheet of paper which has been coated with gelatin, the picture surface and the gelatin being moist at the time. On drying afterwards, the paper readily peels away leaving the picture in perfect contact. The first method, when the surface upon which the picture was developed forms the final resting place for the image, is termed 'single transfer'; and the second, when such support (termed 'temporary support') is only an intermediary, the image being transferred to another medium, is called 'double transfer.' It will be seen that in the first case, the image is laterally inverted and if such inversion be objectionable a reversed negative must be used. But in many cases—as for example, in studio portraiture—it is not convenient to make reversed negatives, and so the double transfer process must be used.

In order to secure adhesion of the exposed tissue to the support it is necessary that its outer margin be tacky. The gelatin must, therefore, be unacted upon. This is secured by rendering the margin of the negative opaque either by means of black varnish or by opaque paper applied to the glass side. This is termed the 'safe edge.'

When the exposed and moistened tissue is 'squeegeed' down upon glass all air between the surfaces is excluded and they adhere by atmospheric pressure. Any smooth impermeable medium may therefore act as a temporary support. Finely ground opal glass is the most

generally used, the white surface being an advantage because it enables the printer to judge when development is complete. The opal receives a preliminary film of wax and resin and upon this surface the carbon tissue is developed. If, however, the film is to remain on the opal this treatment is omitted.

The final support for the image in the double transfer process is generally paper, which is prepared by coating the surface with gelatin containing a small quantity of chrome alum. The carbon image is moistened together with this paper and the two are brought into intimate contact by the squeegee. The two surfaces adhere so tenaciously on drying that when the paper is pulled away from the support the image is found to be firmly attached. Instead of opal glass a temporary support of paper may be used (Sawyer's temporary flexible support), prepared by coating strong paper with a solution of gelatin containing chrome alum, and, after drying, with an aqueous alkaline solution of lac. The paper is afterwards rendered smooth by calendering. Such support is very convenient, and must be used when it is desired to transfer the image to a *rigid* final support. When a reversed negative can be employed, the image may be developed directly upon the paper which forms the final support. Such paper is first rendered impermeable to air by coating with gelatin solution containing chrome alum, and such coating, when dry, is insoluble in the hottest water ever required for development of the tissue.

As carbon tissue shows no visible change on exposure, the time is determined by trial, an actinometer being used, the indications of which serve for subsequent prints, when the correct exposure has once been found. The precise procedure for the production of a carbon print by the simplest process, that of 'single transfer,' is as follows: the negative first receives a safe edge and a tissue is exposed for the correct period. A sheet of transfer paper previously well soaked in cold water is placed in a tank of water at ordinary temperature and the exposed tissue is introduced and this, when moist, is brought exposed side down upon the transfer paper, the two are withdrawn and placed upon a flat surface and squeegeed together, after which they are allowed to stand under slight pressure for 10 minutes. The mounted tissue is afterwards put into water at 35°. When the soluble gelatin oozes from the edges of the tissue, the backing paper is gently pulled away and water is carefully laved over the surface, until the image is fully developed. The print is then rinsed in cold water. It is now placed in a 2½ p.c. aqueous solution of alum for a few minutes, after which it is washed again in cold water and then dried. The dried picture is ready for mounting or may be kept unmounted. The procedure is identical for double transfer pictures developed upon a temporary support. To transfer to the final support the picture is, after drying, soaked in cold water . . . . . The final support, which has been soaked in cold water until quite soft, is placed together with the print in water at 25°, where they remain for a brief period. The final support is adjusted over the image, the two are removed in contact, 'squeegeed,' and



allowed to dry, when the transfer paper can be pulled away and will carry the image with it.

*Indirect processes for carbon printing.* A process termed 'ozotype,' introduced by Manly, enabled carbon prints to be produced without the direct exposure of the tissue to light. A sheet of sized paper is coated with potassium dichromate and a manganese salt and dried. It is exposed under the negative and from the appearance of the visible image the duration of exposure required is judged. The printed sheet is washed in water and dried. A piece of carbon tissue or, as it is termed by Manly, 'pigment plaster,' is soaked in an acid solution of a reducing agent, and this is squeezed into contact with the print. The combination is allowed to stand, after which the 'pigment plaster' is developed in the same way as an ordinary carbon print. The reducing solution used is composed of copper sulphate, quinol, acetic acid, and glycerol, in water.

Another method due to Manly and largely used is 'ozobrome.' A print from the negative is first made upon silver bromide or upon so-called gas-light paper (see page 229) which is thoroughly washed after fixation, hardened in formalin solution, again washed and dried. A sheet of pigment plaster is soaked in a solution of potassium dichromate, ferricyanide, and bromide, and is brought into contact with the face of the bromide print which has previously been soaked in water. The two are squeezed together and allowed to remain for about 10 minutes. The subsequent operations of development may be performed on the print. The print may be developed *in situ* on the bromide print, or the acted-upon tissue is pulled away and is squeezed down upon transfer papers. In both cases, development is the same as for carbon printing. If the latter plan is adopted, the bromide print can be utilised again, if it is well washed and subsequently redeveloped. When the carbon print is developed directly upon the bromide print, the bleached image—which results in the process—is removed by means of a solution of sodium thiosulphate and potassium metabisulphite, and is washed in water.

In this process gum arabic replaces gelatin. The sensitive surface is prepared by coating paper with a solution of gum arabic, potassium dichromate, and pigment. The paper is exposed under a negative and after development is removed by washing in warm water, the soluble portion being removed by attrition. In this method, the rendering of gradation is imperfect, but the results in the hands of tasteful and capable workers are frequently very pleasing.

*Oil Printing.* A sheet of dichromated gelatin-coated paper is exposed under a negative, washed in cold water and dried. It is then soaked in water until the image is in relief, when the print is removed and the superfluous water removed by a clean cloth. If a brush charged with a varnish pigment (lithographic printing ink) be applied to the damp print with a dabbing motion the ink will be taken by the tones of the print in proportion to the degree of insolubility—in proportion to the light action. A slow motion of the brush will deposit ink which may afterwards be partially or entirely

removed by a more rapid dabbing action. Inks of different degrees of stiffness are required and much skill is necessary in the inking.

Oil printing is identical with the Colotype process (see page 230) with the 'Bromoil' is a printing process introduced due to C. Welborne Piper. A finely prepared silver bromide print is treated with a solution which is identical with that used for the ozobrome process (*v. ante*), but containing in addition ordinary alum and citric acid. The print—which is bleached by this solution—is treated with dilute sulphuric acid followed, after washing, with a solution of sodium thiosulphate and is again washed. After removal of the superfluous water, the print is ready for inking (pigmenting) after the manner briefly described under oil printing. A considerable number of modifications of the first (bleaching) solution have been proposed and used.

*Bitumen.* The changes which are produced in dichromated proteids and carbohydrates are not only utilised in pure photography, but have very important application in photo-mechanical printing surfaces which are described below. Prior to their use for the purposes detailed, bitumen was employed, which did not, however, offer the same opportunities.

Bitumen of Judaea (see vol. i. p. 314), if exposed in thin films to light, becomes so changed that it no longer dissolves in turpentine, and this enables it to be used in the making of line and half-tone relief blocks and in photo-lithography. A solution of bitumen in benzene is applied to the surface of a polished zinc plate, and after exposure under a suitable negative is treated with turpentine. The unexposed parts dissolve away, leaving an image in insoluble bitumen, which is capable of protecting the metal from the action of the mordant and furnishes therefore the means for etching into relief as described under the heading of *Line etching*.

If the bitumen, as it occurs, be powdered and digested with ether, a portion of the mass is dissolved leaving an insoluble residue which is soluble in turpentine. A solution made from bitumen so prepared yields films of a much higher degree of sensitiveness than ordinary bitumen. In spite of this and of other methods (combination with sulphur) for enhancing the sensitiveness, the body is relatively insensitive as compared with dichromated mixtures and is now practically out of use except for certain photolithographic processes.

#### SURFACE PROCESSES.

*Photo lithography.* A lithographic print is a picture in varnish-in. The surface of a calcareous stone is treated with the design upon the stone which produces its selective attraction for the ink upon the inking roller is produced by drawing upon the surface with a fatty medium, but the original design may be copied by photography and transferred to the stone from which prints may afterwards be produced. Such copies are photo lithographs. Any drawing in pure line or in continuous tone may be reproduced in this way. Two methods are adopted—direct and transfer. The negatives most suitable for the production of prints in line are made by the

collodion process. The negatives must be reversed. For the 'direct' process the surface of a well-polished lithographic stone is warmed and is then coated evenly with a solution of fish glue (or albumen) and ammonium dichromate in water. The film should be thin. After drying the stone is ready for exposure. For small subjects an ordinary glass negative may be used, which is pressed into contact in a specially constructed frame with plate glass front. It is more satisfactory, and is indeed necessary with large sizes, to use thin film negatives, which may be arranged on the plate-glass bed of the frame over which the stone is then placed. To avoid the cost and inconvenience of larger frames, the film negatives may be gently 'squeezed' into contact with the sensitive surface, using as a cementing medium a solution of mineral oil in naphtha, all traces of which may afterwards be removed by treatment of the surface by naphtha, followed by benzene, without damage to the exposed sensitive coating. The film negatives which should be collodion films, strengthened before removal from the glass plate by coating with a solution of rubber in benzene have no 'spring' and adhere easily.

After suitable exposure the surface of the stone is coated by means of a composition roller with a thin film of lithographic transfer ink thinned with turpentine or naphtha. After evaporation of the solvent the surface of the stone is flooded with water. On gently rubbing with a tuft of cotton wool the unaffected portions of the coating wash away carrying their covering of ink, and there remains an image of the insoluble fish glue bearing upon its surface the coating of the fatty transfer ink. The stone is then covered with a solution of gum arabic in water which is allowed to dry, after which it is preferably allowed to stand for a few hours, when it is ready for the lithographic printer, to be 'rolled up' with lithographic printing ink, dusted with resin which adheres to the ink image, etched with very dilute nitric acid, 'washed out' with turpentine and again rolled up with ink, when an impression may be taken in the lithographic plate. The ink and additional matter may easily be put upon the stone. The effect of the treatment to which the stone has been subjected has been to form upon its surface an image in fatty salts of calcium. This image rejects water whilst the unaffected portions of the stone hold water. If while the surface is in a damp condition, varnish ink (pigment and linseed varnish) be applied, such ink will be deposited upon the image but not upon the damp portions of the stone where no fatty salt has been formed. This, in brief, is the leading principle in the production of an image by lithography. If paper be laid down upon the inked surface and pressure be applied, the ink is transferred to the paper, and the cycle of operations—damping, rolling, and printing—is repeated for subsequent copies.

If the original picture to be copied be in continuous tone, a ruled screen negative (see *Half-tone screen process*) of a particular type is made, which is used for printing upon the coated stone as described. Such process requires considerable attention to details, especi-

ally in the selection of the stone and preparation of the negative, and finds its most useful application, not for monochrome, where the copies tend to show a flat scale of gradation, but for photo-chromo lithography, in which a number of separate impressions in different coloured inks from different stones are superimposed, after the manner of the '... ..' for the production of pictu... .. an original in colour.

In the transfer process a sheet of paper surface coated with gelatin (photolitho paper) is immersed for a few minutes in a 5 p.c. solution of potassium dichromate and afterwards dried in the dark, preferably in a freely moving current of air, in order to ensure rapid drying. It is then printed under a negative (unreversed) of the subject in line to be copied, care being taken to ensure perfect contact of paper and negative, and to avoid undue exposure to light, which causes increase in the thickness of the lines forming the image. After exposure, the sheet is placed on a flat surface and coated with 'transfer' ink by means of a roller, avoiding excess. After evaporation of the solvent, the inked sheet is placed in water at 16° (approx.), where it is allowed to remain for a few minutes, when it is removed and placed face upwards upon a sheet of glass. The unexposed portions of the gelatin absorb water and swell; such action does not take place in the exposed parts to more than an appreciable extent. Upon gently rubbing with a tuft of moist cotton wool, the ink will leave the swollen parts but adhere to the exposed portions. When this process of development is complete there will remain an image of insolubilised gelatin bearing a coating of ink, upon a ground of clean gelatin. This picture—the transfer—is then allowed to dry. It is afterwards damped, when the ink image may be transferred to stone by the usual procedure.

Transfers produced from screen negatives for the production of subjects in continuous tone are only satisfactory when the negatives are made with coarse screen, owing to the tendency of the dots to spread, first in the exposure, afterwards in the inking, and finally in the transfer process.

The advantage of the direct over the transfer process lies in the avoidance of stretch, a necessary consequence with paper, but in ordinary routine work the transfer process is the method most generally used.

*Photo lithography in tone.* A process for the production of continuous tone subjects—nature negatives and copies of drawings—depends upon the fact that if the thickness of the gelatin coating upon a gelatin 'transfer' paper be increased and contain in addition to the dichromate other substances as, for example, sodium chloride and potassium ferri-cyanide, the film, after exposure under an ordinary negative and soaking in water, will swell and reticulate in varying degree according to the amount of light action produced under the different portions of the negative. This reticulation of the transfer means that the film will no longer be continuous in one plane but broken up into 'grain,' and if ink, transfer ink for example, be applied, it will adhere to the image in isolated masses of

varying size, which are capable of producing the illusion of shading. The 'grain' can be varied to suit the subject; and the finer the detail to be rendered, the finer the 'grain' should be. The ink image is eventually transferred to stone (*v. also Collotype*). From the finished stone, transfers can be taken which can be utilised in the production of a series of new stones, which after careful modification by hand can be employed in the production of pictures in colours by chromo lithography.

Photozincography and photoalgraphy are processes in which zinc and aluminium are used in place of the lithographic stone as the printing surface, and the methods employed are similar to those described.

*Collotype.* A collotype print is a picture in varnish ink obtained from the surface of chromated gelatin which is supported upon a rigid body, generally glass. Such a surface is produced by exposing the dichromated gelatin-coated glass under a negative and afterwards removing the unaltered chromium salt by washing in cold water, when the film is dried spontaneously. If the film be afterwards moistened with an aqueous solution of glycerol and ammonia, such solution will be absorbed, and the gelatin will swell slightly. If the excess of such 'damping' solution be removed and a charged roller be passed over the surface, the ink from the roller will be taken by the different parts of the film proportionally to the amount of light action which has taken place during the exposure under the negative, and this ink may be readily transferred to paper by simple pressure. By this process it is therefore possible to render automatically by purely chemico-physical means the gradations of light and shade in the negative in such a form as to be utilisable in the printing press. It is interesting to compare this process with Woodburytype, where the translation is mechanical, and with the half-tone block process, where it is produced by optical means.

Provided that a suitable negative be made, any subject can be rendered in collotype. The plates may be printed in the press, where the manipulations are wholly by hand, or in the machine, where the damping, inking, and printing are mechanical. The rate of printing of the best class of collotype is slow. The process is valuable for the reason that it is capable of yielding pictures the gradations of which are faithful to the negative and, as compared with the half-tone block process, without the disturbing effect of the regular dot formation. The variety of printing paper that can be used is considerable, and because of this fact the process has additional value.

For the preparation of the printing surface a sheet of plate glass,  $\frac{3}{8}$  to  $\frac{1}{2}$  inch in thickness is finely ground upon its surface and is then flowed over with a solution of an alkaline silicate and white of egg. After evaporation of the water, the plate is heated to about 60°. It is then cooled and washed in cold water and afterwards allowed to dry. This process is termed 'substratuming,' and its purpose is to cause a deposit of silica upon the glass. This deposit, in addition to the roughness of the glass, causes the subsequent film of gelatin to adhere strongly. This device is necessary

owing to the mechanical strain upon the film caused by the operations of rolling and printing.

The sensitive film is produced by coating the plate with a solution of gelatin and alkali dichromate in water. The gelatin used must be of high grade and of medium 'hardness' and free from fatty matter. The prepared glass is warmed and levelled, and the requisite quantity of the solution is poured upon the surface and spread, preferably by the clean finger. Drying must take place by evaporation at an elevated temperature—there is no intermediate setting to form a 'gel.' Upon correct conduct of this drying the success of the plate maker largely depends. To this end, the plate rests upon levelling screws in a drying oven, which is a box—generally constructed of wood—large in volume, and kept at the suitable temperature by means of a steam or hot-water radiator. Gas or oil heating may be used, provided that care is taken to prevent the products of combustion entering the chamber containing the plates. The construction of the oven must be such that there is no internal vibration and that there are no 'draughts.' Failing these conditions the film will dry with an uneven surface—a fatal defect. The top of the box must be covered with a fabric which will permit the passage of the water vapour from the plates out of the oven.

The oven temperature, varied between 40°–60°, influences the character of the film. When the film of gelatin is dry the oven is allowed to cool, and afterwards the plates are removed and are kept in the dark. The films will remain in good condition for 1–2 days, depending upon the atmospheric surroundings. If, however, storage takes place in an artificially dried atmosphere, as in a storage box containing a tray full of calcium chloride, the plates may be kept 5–6 days. Deterioration is due to

oxidation of the film. For  
inverted negatives are re-  
the plates are printed  
(exposed), in the case of small pictures, from glass-plate negatives. More perfect contact between the surfaces is obtained by printing from flexible film negatives prepared for the purpose, which are laid upon the plate glass bed of the printing frame. By means of thin tin foil such negatives are masked at the margins to show only the amount of subject required. Exposure takes place in the ordinary way, but the frames have usually no backs, so that the under side of the film may be examined in order to observe the progress of printing. The film darkens in proportion to the duration of exposure. Usually, the printer determines the correct amount required by judgment. When the plate has been exposed sufficiently, it is removed, and is then quickly and evenly immersed in water or it may be flooded. Washing continues until the free dichromate is removed, when the film will be practically without colour. It is then dried. Examination of the plate before drying, at this stage, shows that the image is in slight relief and that it is reticulated. A certain amount of 'grain' is required to ensure successful printing at the press, but such 'grain' should not be obvious to the unaided eye. The following conditions influence the character of the 'grain':

kind of gelatin; thickness of film; proportion of dichromate present; the particular alkaline dichromate used; drying temperature; length of time the plates have been kept previous to exposing under the negative; the after treatment of the exposed and washed-out plates and the addition of special salts, as, for example, calcium chloride and potassium ferricyanide (v. also *Photo lithography in half-tone*). For special purposes—for example, amongst others, the means of making transfers for half-tone—plates are specially prepared to give the best results from one or of the last two named substances, although this is not the only method, nor are they when used the sole determinants.

**Printing.** The plate during printing must be in a damp condition. This may be secured by simple water damping, but when water alone is used, frequent application is necessary, which makes print making a slow process, and moreover is useable only for hand-press print. Generally water containing a hygroscopic substance as, for instance, glycerol or calcium chloride, is used with addition of ammonia which softens the film. When the film is in a sufficiently moist condition, the superfluous solution is removed, the plate is ready for the press or machine. During printing, the damping solution is re-applied to the ink-free film as required from time to time.

The printing inks used must be specially prepared from *finely ground* lakes and other suitable pigments. No body of a gritty character should be used. The medium should be linseed varnish of high quality: non-drying oils and fatty matter must be avoided. As the film of ink allowable upon the image is very thin, the medium should be 'loaded' with pigment and in consequence collotype inks of high grade are very stiff. For use, the printer employs as reducing agent when required 'middle' and 'thin' linseed varnish.

The rollers used are leather, 'nap' and smooth, and also gelatin composition. A nap roller, charged with stiff ink, is applied to the plate and with frequent rolling the dark and middle tones are produced, after which the smooth leather or composition roller, covered with thinner ink, is used for the more delicate gradations. After inking, the ink from the plate is transferred to the paper (or sometimes a fabric) by pressure. The paper used must be of absorbent nature and of medium hardness. (Given these conditions, considerable variety is possible.)

**Collotype in colour.** If the grain of a collotype is fairly pronounced, it is possible to transfer a printed image to a lithographic stone, and by such means beautiful colour work has been done. For such productions, plates are specially prepared from negatives which have received considerable modification (by retouching and masking), so that the gradations are made to coincide as far as possible with the amount of particular printing colours required for any region, when superimposition of the different printings will yield the hue required. The stones forming the series for any picture require considerable correction at the hands of a competent lithographic draughtsman, and it is largely owing to his skill that good results are

due; hence the process, although interesting, is little used.

Another method is to print from several plates in separate colours from different negatives which have been modified by hand work, superimposing the coloured impressions. The most perfect method where collotype is used is to produce one or two of the necessary printings from collotype plates, generally in neutral tints, and to complete the picture by hand-drawn lithographic stones. This process yields in general very beautiful results. Collotype has been employed also in the three-colour process—for which it is, *ab initio*, unsuitable.

Collotype pure and simple, by reason of the fact that a printing surface of damp gelatin is used—which is liable to be affected by changes in the hygrometric condition of the atmosphere—is a process difficult to work so as to produce very uniform results. Whilst slight variations are not serious in monochrome printing they become so when colour work is attempted. For this reason, mainly, collotype in colours is difficult and in consequence the products are relatively costly.

#### RELIEF PROCESS.

In the pictorial representation of any object the form is rendered either by pure line, as in simple pen and ink drawing where the lines may be assumed, for simplicity's sake, to be all of uniform depth of colour, or by patches of pigment of varying intensity, either in monochrome or colours, as in a wash drawing or in an oil painting. The former may be termed 'broken' tone and the latter, 'closed' or 'continuous' tone. A third division is formed by a combination of both these methods—a picture may be formed of washes of pigment in conjunction with pure line. An impression in printer's ink from a form of type matter (the page of this book for instance) is an example of broken tones: the transition from ink to paper is abrupt. A photographic portrait is in continuous tone, there is no discontinuity in the shading by which the form of the person and the background is represented.

In the copying of which forms a very important part of the work of the photo engraver, are not always strictly 'broken tone.' In certain cases they are so, as for example, in the so-called mechanical drawing, where the lines are of uniform intensity, and also in many other expressions of the pen of a formal character. Of these it is possible to produce fine results, but in work of a more pictorial character, the definition given does not apply, for the reason that there is shading even in the lines themselves and much of the beauty of the drawing depends upon such variation. The character of the work of fine engraving renders drawings of this character imperfectly, for in the rendering, the forms of the lines only are given, and not the variation in their tone. All the lines in the drawing are reproduced in the printing block, correct in form, in relief and in the same plane. When the printing roller passes over the surface all the lines receive ink to the same amount for equal area, and this ink is eventually delivered to paper. The consequence is that lines of different intensity in the original are represented as the same intensity in the copy, with

falseness of effect as a result. It is possible by modifying the lines in the etched relief plate by means of the graver to vary the area of metal and thus to vary the amount of ink delivered to the paper, and in this way to alter the intensity of the printed line. For example, a line which prints too dark may be reduced in width, may be split or cut up into dots. In any of these alternatives the effect will be to show a lighter tone in the print. By such means a facsimile of the effect of the drawing is possible, so that to the eye the copy appears as the original drawing. In order to produce a rendering of the continuous tones or shading of a wash drawing or a nature photograph by means of a type-high printing block, it is necessary to have recourse to a device. This device depends upon the fact that if there be placed upon white paper a regularly disposed series of black dots, the assemblage when examined at such a distance that the angle subtended by the major diameter of the individual dot is exceedingly small, the eye is unable to distinguish between dot and interspaces and, as a consequence, the illusion of a shade of grey is produced; the depth of the tone depending upon the proportion borne by the area of the black to the area of the white. If the dots are disposed with perfect regularity and are uniform in size, then the tone produced will be uniform over the area, but any variation either in disposition, size, or intensity of the black dots, will result in tone difference. Assume, for the moment, that blackness and disposition are uniform, then variation in size will admit of there being produced a variation in the shading. If a series of tones, say a simply graduated patch of black to white, produced by washing lamp black upon white paper, be imitated in effect to the eye, by applying the foregoing principle, the 'continuous' tones of the patch are said to have been translated into 'broken' tone. The effect in the case of the lamp black wash is due to varying absorptions of the incident light by the varying amounts of the pigment; but in the other instance, the effect is produced by an illusion—by the optical dilution of white with black to produce different shades of grey. The use of this principle is common in graphic arts. It is used by the pen draughtsman, as is seen in steel engravings, in the stipple work of the lithographer and in the shading produced by the juxtaposition of mechanically engraved lines of uniform or varying width and distance apart, which the wood engraver, for example, in the pictorial machinery.

Given the dot translation of the graded black and white patch it may be photographed in the same manner as a type-high and a type-high block produced in similar fashion.

Prior to the period when the modern method for the rendering of gradation was introduced, broken tone pictures were prepared to give a semblance of shading by a method of drawing upon paper with a paste coating which had been impressed with a grain, regular or irregular, while the surface was in a plastic condition. The draughtsman drew upon this surface with a lithographic crayon, simulating the shading of the original drawing, which was possible by varying the pressure upon his crayon. The

absence of planarity in the surface gave isolated patches (irregular dots), instead of smooth tones, which would have been produced had the surface been flat. The finished drawing could now be photographed, transferred to metal by printing by the dichromated albumen process, and afterwards etched type high, or the drawing so made could be treated as a lithographic transfer—the image could be transferred to stone and printed lithographically or to zinc and printed in the same way. Again, if it was transferred to zinc of suitable thickness, it could be etched into relief and printed by letterpress.

Another phase of the same plan consisted in employing chalk-coated paper upon the surface of which was printed a series of fine lines close together, or a fine, regular, or irregular stipple in black in addition to the impressed grain. These were known as 'scraper boards.' The surface of the sheet presented, when examined at the normal distance of vision, a uniform light grey tone. Drawing was effected in the way described, and the coating could be scraped away, so lightening any part. The printed tint saved work in drawing. All parts of the board not touched by the draughtsman remained in semi-tone and this, when contrasted with the high light and shadow, gave the opportunity of suggesting the presence of middle tones by the expenditure of less labour in drawing than would have been necessary had the tint been absent. Scraper board was, at one time, employed for the majority of fashion plates and other drawings for commercial purposes. The illustrations, Figs. a, b,

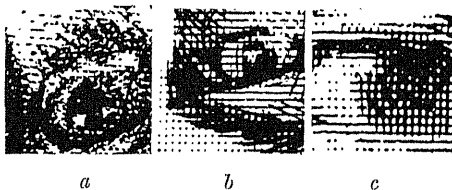


FIG. 9.

c (Fig. 9), are slightly enlarged representations of portions of drawings produced by this method.

Modern photo engraving, however, dates from the introduction of a more facile method of translation, which is the optical method of Ives. Such translation is effected in the negative in the manner to be described.

#### PROCESSES.

**Line.** The initial stages in the production of a relief block of a line or other 'broken' tone drawing are identical with those for the making of a direct photo zincograph (*v. ante*, *Photolithography*) and are directed to the making of a fatty ink image upon the surface of a sheet of zinc. Provided that the metal be sufficiently thick, the image produced for lithography (actually zincography) may be etched into relief, or the image produced for relief will serve equally well as the starting-point for lithographic printing.

The processes of line etching now in general use are known by the names of the 'roller' process and the 'dragon's blood' process. Both

of these require a print upon the surface of zinc which is prepared by exposing the metal, coated with a very thin film of albumen (or fish glue) and all dichromate, under the negative

The exposed print is covered with a thin film of greasy ink, the plate developed in water, and when dry the image is dusted over with finely divided bitumen, which adheres to the ink lines. The excess of the powder is then removed, leaving the metal clean. The plate is now warmed, when the bitumen melts and incorporates thoroughly with the ink. The resist which results is satisfactory for the roller method, but for the 'dragon's blood' process the 'transfer' ink used for coating the exposed albumen plates is replaced by a harder and more wax-like ink, and the resist produced is capable of standing a more prolonged etching, which is an advantage in that more relief is produced with which to commence the characteristic operation of the process. The enameline process (see *Tone process*) is also used for the making of the resist for dragon's blood etching. In the roller method, the procedure, after the resist is made, is as follows: The plate is placed for a minute or so in a 1 p.c. solution of nitric acid for the purpose of removing any traces of dirt from the bare parts of the metal, after which it is washed and then wiped over with a sponge charged with a solution of gum arabic. The plate is now rolled up in the lithographic manner with a roller charged with the so-called 'starting' ink which is usually composed of letterpress ink, beeswax, and lithographic varnish. When the image is strengthened by this 'rolling up,' the plate is dried and is then dusted with resin—usually dragon's blood is used—after which the plate is again placed in dilute nitric acid, where it remains until a slight relief is obtained for the covered parts of the metal. The plate is washed, dried, and heated slightly, the effect of which is to cause the wax in the ink to run over the exposed edges of the lines—an operation requiring skill and experience—and the plate is then cooled.

This cycle of operations is repeated usually four times, increasing at each repetition the concentration of the acid, the amount of ink, and the degree of heating of the plate. After the operations described are completed the plate is cleansed. Examination will show that the lines in relief have sloping sides with a step-like formation as shown in Fig. 10. The 'steps'

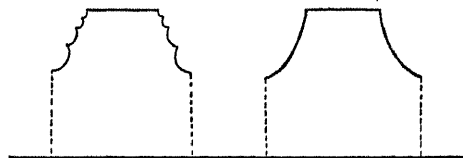


FIG. 10.

are due to the successive meltings of the ink and subsequent etchings, and are only slightly evident if care and skill are employed by the etcher. These steps are to be removed so that the lines may have smooth sloping sides. If the running of the ink has not been properly performed so that the sides are unprotected, they will be eroded or undercut, and as a result the

lines will break away in the etching bath or at the least be defective and an imperfect rendering of the drawing will be given. The steps or 'shoulders' to the lines are removed by the operation of 'finishing.' A hard, glazed leather roller is charged with a strongly resisting ink (composed of good lithographic printing ink, beeswax, and bitumen) and with this a thin film is applied to the surface of the lines of the previously cleaned plate, after which the plate is placed in dilute nitric acid. This removes the 'step' near the surface of the line. The plate is washed and dried and again rolled up, but this time the roller is pressed down during rolling so as to coat the straight edge of the side of the line left by the first finishing bath and the plate is again etched until the remaining 'shoulder' is removed.

In the dragon's blood process, the plate is given a first etch for a longer period than in the roller method. The subsequent protection of the sides of the lines is effected by what is called a 'banking' of the resin. This banking is made by brushing across the plate, by means of a large flat brush, finely powdered dragon's blood which is, by reason of this operation, mechanically held against that side of the line which faces in the opposite direction to that in which the brush is travelling. The amount of banking is varied by the angle at which the brush is held. When the excess of resin is removed the plate is gently heated, when the resin melts sufficiently to stick to the metal, after which it is cooled. The 'banking' is repeated from the remaining three sides of the plate, so that every line, in no matter what direction it may be, receives protection. In some cases, extra 'bankings' may be wanted. The plate must not be heated sufficiently to cause the resin actually to flow. After the sides of the lines are protected, the plate is etched, when the banks of resin gradually break away and the edges of the lines begin to be exposed. The plate is washed, dried, and the protection of the sides again performed, and the etching repeated. These operations are continued until sufficient relief is obtained. To secure adequate protection for the surface of the lines, the plate is usually rolled up once with a resisting ink, the resin afterwards adhering to this, and when the plate is heated incorporating with it.

After the main etching, the plate is cleaned, and then may require a 'finishing' bath, but the 'finishing' is not required to the same extent as in the plates produced by the roller process.

Etching is generally performed in large earthenware troughs supported upon rockers, by which a see-saw motion is given, but it is becoming now the practice in large establishments to etch by means of etching machines which mechanically deliver a spray or stream of acid against the plate. The etching is more quickly performed, and there are attendant technical advantages. The powdering with dragon's blood may now be done by a special machine.

The advantage of the dragon's blood process lies in its speed and ease, compared with the roller method.

Where there are large areas of bare metal, it is necessary to obtain considerable depth, the actual depth being mainly dependent upon the

width apart of any two contiguous ink-bearing portions standing in relief. The removal of the metal by etching is lengthy, and is, moreover, wasteful of nitric acid. In modern practice, it is the custom to avoid, as far as possible, this 'deep' etching by removing the metal in the more open spaces by means of a rapidly rotating cutter in the 'routing' machine.

The etched plate is afterwards trimmed, and is then mounted upon a block of oak or mahogany 'type high,' when it is ready for the printer. The satisfactory mounting of the plates is one of the most serious problems of the block maker, there being at present no entirely good method.

*Tone processes* ('half-tone' or 'process' blocks). In these processes we use the principle of translation of continuous tone into broken tone described. Any picture, whether drawing or photograph, may be represented by the half-tone process, which is the most common of modern illustration methods. Given a picture, such constitutes the starting-point, but if an object in relief is to be portrayed, an ordinary photograph must first be made. Except in certain cases—where the range of contrast in the subject is slight—this is the rule. Such photograph is the original. A secondary negative is now made—the original is again photographed—and it is in this second photograph that the translation of tone is made into dot and from this negative the metal printing-surface is produced.

To produce the half-tone negative there is placed, some little distance in front of the sensitive plate, during the exposure in the camera, a sheet of glass having a large number of small apertures, the effect of which is to translate or break up the shading of the ordinary photograph or drawing into dots of various sizes in proportion to the brightnesses of the tones. This glass plate is termed the 'ruled screen.' It is formed of two plates of flat transparent highly polished glass which are cemented into optical contact. These have, upon their inner surfaces, a series of alternate opaque and clear lines which are usually of equal width, and their direction forms with the sides of each plate an angle of  $45^\circ$ , but from different sides with the two plates. The result is that when the plates are in contact there is produced a series of square transparent openings. The number of lines to the linear inch with different screens varies from 50–250 and as the spaces and lines are equal we have lines equal to  $\frac{1}{500}$ th to  $\frac{1}{250}$ th in. The effect produced by the different rulings when the screens are used for negative making is to give a variable number of dots to the superficial inch, each dot corresponding to an opening. The greater the number of dots upon unit area the finer the gradations (detail) in the translation. It may, however, be taken that for few subjects it is necessary to use screens having rulings finer than 175 lines to the inch.

Such screens are made by coating the surface of glass with a resisting medium which is afterwards cut away by the use of a diamond point in a special form of ruling machine leaving the glass exposed. Afterwards the plate is subjected to the action of hydrofluoric acid, the resisting medium is cleared away, and the etched lines

are then filled in with a black pigment. On completion, there is shown a series of opaque lines upon a transparent ground. Two such plates cemented in contact form the screen, the appearance of which is shown by Fig. 11.

The placing of the screen is not a matter of simplicity, so far as its distance is concerned. It is necessary that the position be chosen after consideration of the camera extension, the lens aperture, the screen ruling, the subject and the negative-making process, which is most usually wet collodion. If the screen be placed in close contact, dots will be produced, but they will be of equal size, and all gradation of tone will be lost. The dots will also be variable in density with this uniform size while they should be variable in size and uniform in density. If the screen be placed too far away the sizes of the dots will not be correct. In the case of too great distance, the effect of the screen for some tones will be lost, the tones will be continuous again and if a further distance than this be taken the effect of the screen will be wholly lost. In such a position the screen acts, to all intents and purposes, as a sheet of neutral-tinted glass. The success of the process in

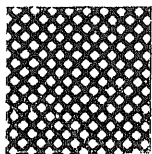


FIG. 11.

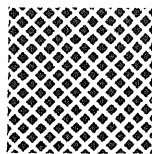


FIG. 12.

practice depends, after correct distancing of the screen upon exposure (which is made in part with one aperture of small size and in part with one of much larger opening—a plan which is necessary in all cases where there is any considerable range of contrast in the original) and upon the processes of development, reduction or clearing and intensification which follow.

From the negative the print upon metal, which is to form the resist to the etching mordant, is prepared. Usually, for the best class of work, half-tone blocks are prepared upon copper, and the process employed is that known as the 'enameline' or 'fish glue' method. A sheet of polished copper is coated with a viscous solution composed of fish glue (gelatine) and an alkali dichromate in water, and the resulting film is dried by gentle heat. The coated plate is exposed under the negative, when the portions exposed to light change and become insoluble in water, whilst those parts under the dots remain unaffected and so retain their solubility. After exposure, the plate is washed in cold water until all the soluble portions are removed when the plate is dried. There is now on the surface of the metal a print, the tones of which are produced by dots of various sizes. The metal is strongly heated, when the print changes in character, becoming hard and enamel-like, in which condition, when cool, it is capable of withstanding the mordant—ferrie chloride—which rapidly attacks the uncovered metal. Upon etching the protected parts are left standing in relief, the necessary condition for



the printing press. In most cases, the automatic process is assisted by a process of selective or 'fine' etching. If the tones in any part of the plate are not such as will give the desired shades, if for example, the dots are too large, which means too dark a shade in the print, the remaining portions of the etched plate are covered over by a resisting medium applied by means of a brush and the plate is submitted to a further etching. It will be noted that in the description, no mention is made of any protection to the sides of the dots as the etching proceeds, whilst reference to the explanation of the mode of producing line plates will show that elaborate precautions are taken to such end. The actual 'depth' or 'relief' required in a half-tone block is extremely small, for the reason that the ink-bearing elements—the dots—are very close together. But lateral action does take place, with the result that, owing to under-cutting, the size of the dot portion decreases and as a consequence the ink-bearing capacity is lessened and so the dot prints lighter. Allowance is made for this in the negative, so that the printed dots on the metal are larger than are required in the finished plate. Upon this lateral action, modification of tone by 'fine etching' depends, for, if the re-etching for any tone be carried far enough, the tone may be brought to almost any degree of lightness of shade. After completion of the etching, the plate is cleaned and is mounted type high upon wood.

The continuous tones of a picture may be translated into isolated elements of a less regular order than obtains with the use of the ruled screen, by means of a special form known as the 'metzograph.' This is a plate of glass upon the surface of which pyrobetulin has been deposited by sublimation. The coating so produced takes a vermicular form and the surface is afterwards etched with hydrofluoric acid when the glass assumes a similar character, presenting a series of minute cavities, the number per unit area on the 'coarseness' of the screen can be varied. Such a plate appears to the eye faintly translucent. If it be placed in front of the sensitive surface during exposure, the tones are broken up into isolated particles which are distributed with extreme uniformity but without the mechanical regularity of the ruled screen image. The particles vary in size and shape and the absence of the definite and regular dot formation is an advantage in the reproduction of many classes of originals. The negatives are employed in the same way as those made by the ruled screen. The character of the 'texture' produced by the two methods is shown in Fig. 13, *a* and *b*, by which comparison may be made.

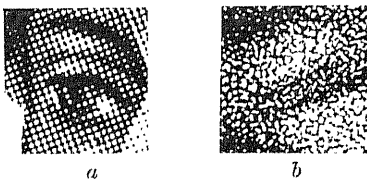


Fig. 13.

*Three-colour printing by relief blocks.* The principles upon which colour is rendered by the

so-called 'three-colour' process are given under the heading of colour photography (*v. ante*), and it is only necessary here to show how these principles are utilised in the making of prints by letterpress. Briefly, the method consists in making three negatives through colour screens, one for each of the fundamentals, and from the negatives, blocks are prepared which are printed on the principle of superimposition in inks approximately complementary to the sensation hues.

Two processes are employed, the indirect and the direct. In the former, ordinary continuous tone three-colour negatives are made, and from these transparencies by contact from which the three half-tone dot negatives are produced. Or, in the direct process, the dot negatives are made direct from the object upon special dry plates which are panchromatic (*see Orthochromatic photography*) and also suitable for ruled screen negative making. Frequently such negatives are made upon panchromatic collodion emulsion. There is a slight complication in making the negatives owing to the fact that if there be printed two or more impressions one above the other from half-tone blocks (or indeed from a ruled screen surface where the colour is in the form of elements in perfectly regular order), a pattern is produced—the so-called *moiré* effect—which is very objectionable. This pattern cannot be avoided, but it may be reduced to an almost negligible form if it be arranged that the lines of dots (forming the half-tone picture) in the separate printings cross at a particular angle which is secured by the positions of the ruled screen when the negatives are made. The direct process is only applicable to the photography of flat objects. If the object is in relief the indirect process must be employed. In any case, the negatives forming the set must have images accurately equal in size. Blocks are prepared upon copper by the enameline process. Successful three-colour work is very largely a matter of skilful fine etching, but the amount required is frequently in excess of that which would be required were more care bestowed upon the making of the negatives. The plates, when finished, are accurately trimmed and mounted, and are afterwards printed in ink of the hues yellow, crimson, and greenish blue. At the present time, the sensitive plates obtainable well fulfil the theoretical requirements, but the same cannot be said of the printing inks.

On the Continent more than in Great Britain and the United States, at the present time, a four-colour process is employed with considerable success. A set of blocks is prepared by the three-colour method and a fourth block is made from the original from a negative made through the ordinary 'yellow' screen, which is employed for the additional printing, the colour being generally a grey of a tone to suit the subject. The extra printing from a block prepared by skilful hands is a valuable aid and serves to soften the crudity of colour which is so frequently a fault in pictures produced by the orthodox three-colour process.

*Preparation of drawings and photographs.* The translation of any picture by screen methods



always leads to a *fine etch* contrast. Although 'fine etch' plates is to a considerable extent employed to alter the appearance of the pictures as presented by the proofs from the plates—of illustrations, indeed, which are not satisfactory to those who wish to use them even before they are reproduced—the process would, to some extent, be necessary in the case of good originals because of the flattening effect of the screen. When drawings are to be reproduced by these methods and have to be made for the purpose, allowance is generally made for the reduced contrast by forcing the effect in the drawing, hence 'drawings,' for process, which are generally made in monochrome body colour although useful for the purpose intended, are of little value afterwards for obvious æsthetic reasons.

Any drawing in line, even those made without any regard to reproduction processes, where beautiful effect is the only consideration, may be successfully translated, but only by the expenditure of extra time and skill. Disregarding pictorial drawings, much technically unsatisfactory 'copy' is dealt with in the ordinary way. When drawings in line are made, however, with a view to reproduction in the commercial way, they are generally prepared in black line upon white card.

By far the larger amount of half-tone illustrations to catalogues (especially those showing machinery) and *photolithography* a similar commercial character are prepared from photographs which have been 'worked up' by the draughtsman.

The appearance of the original by suppression, or by addition, and this to such an extent that the photograph is completely changed. Such 'working up' is carried out by means of the 'air brush,' a pen-like tool by means of which a fine stream of air can be caused to project a spray of liquid pigment upon a surface, the effect producible being entirely under control, and moreover—which is the important feature—with that smoothness and continuity which is a characteristic of the shadings in print. It is largely owing to this that the engraver has almost entirely replaced the wood engraver in the preparation of the illustrations for the best classes of catalogue.

C. W. G.

#### PHOTOLITHOGRAPHY *v.* PHOTOGRAPHY.

#### PHOTOPHONE *v.* SELENIUM.

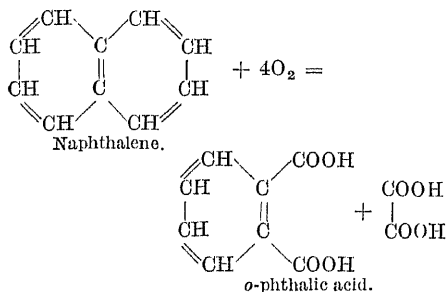
#### PHOTOSANTONIC ACID *v.* SANTONICA.

#### PHTHALEIN DYES *v.* TRIPHENYLMETHANE COLOURING MATTERS.

**PHTHALIC ACID.** The three dicarboxylic acids of benzene are known as the phthalic acids. Of these the only one of technical importance is *orthophthalic acid*  $C_6H_4 \begin{smallmatrix} \text{COOH (1),} \\ \text{COOH (2)} \end{smallmatrix}$  and this is the compound which is always understood when the name *phthalic acid* is used without further qualification, the meta-compound being distinguished as *isophthalic acid* and the para- as *terephthalic acid*.

*orthoPhthalic acid* was first obtained by Laurent in 1836 by the oxidation of naphthalene (Annalen, 19, 38), and the same coal-tar product

has always served as the chief source of this valuable acid—



Similarly other di-substitution derivatives of benzene containing carbon chains or groups in the *ortho*-position yield phthalic acid on oxidation, *e.g.* in addition to naphthalene cited above, tetrachloronaphthalene, alizarin, purpurin, *o*-toluic acid, have been employed, along with such oxidising agents as dilute nitric acid, alkaline permanganate, chromic acid, sulphuric acid (Marignac and others, Annalen, 42, 215; 66, 197; 75, 12, 25; 130, 334; 144, 71; 148, 60; Ber. 6, 945; 7, 1057; 12, 579; 18, 1499; Zeitsch. Chem. [ii.], 4, 551, 705; Compt. rend. 56, 82; Frdl. 1897-1900, 664).

A variety of other methods are known, *e.g.* the action of potassium f... sulphuric acid on salicylic... and sulphuric acids... reaction of resorcinol and... by the reaction between benzyl chloride, carbon tetrachloride and nitric acid; or by acting upon benzene or benzoic acid with pyrolusite and concentrated sulphuric acid in the cold.

Häussermann (J. 1877, 763, 1158) describes a method suitable for laboratory preparation, from 2 parts of potassium chlorate in 10 parts of commercial hydrochloric acid and 1 part of naphthalene, which mixture is gently heated, chlorination first taking place and then oxidation. The product is washed with water and with light petroleum, and afterwards 10 parts of nitric acid (sp.gr. 1.45) is gradually added and the mixture boiled. When all dissolves, the nitric acid is evaporated and the residue distilled; phthalic anhydride passes over, which may be further purified by sublimation, and reconverted into phthalic acid by boiling with caustic soda and acidifying the cold solution with mineral acid. The precipitated phthalic acid is best purified by recrystallising from boiling water.

**Physical properties.** It exists in trimetric plates; whole crystals melt at 213°; when powdered, at 205°, passing into the anhydride, Sp.gr. 1.585-1.593; 100 parts of water at 14° dissolve 0.54 parts of acid, and at 99° 18 parts of acid (Graebe, Annalen, 1887, 238, 321). Phthalic acid is readily soluble in alcohol, sparingly so in ether and insoluble in chloroform (hence separation from benzoic acid); it is slightly volatile in steam. The acid shows an absorption band in the spectrum, but the anhydride does not. It is said to form a eutectic mixture with its anhydride (de Stadt, Zeitsch. physikal. Chem. 41, 353). For measurements of conductivities reference should be made

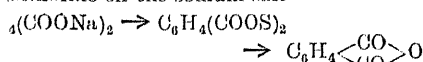
the work of Jones (Amer. Chem. J. 42, 520; 187; 44, 159); Sidgwick (Chem. Soc. Trans. O, 97, 1677); Godlewski (Chem. Zentr. 1904, 1275).

**Chemical properties.** Phthalic acid forms a characteristic, sparingly soluble barium salt (ius, Annalen, 1868, 148, 60; Hermann, ialen, 1874, 171, 78), and also forms salts with most metallic oxides, including bismuth, ium (J. pr. Chem. [ii.] 74, 142; Bull. Soc. n. [iii.] 31, 135; J. Russ. Phys. Chem. Soc. 42, ). Calcium phthalate on heating gives benzo- none, benzene, carbon dioxide, small quan- ties of other hydrocarbons and anthraquinone. The acid itself, when heated with excess of lime, gives benzene and calcium carbonate, calcium zolate being formed as an intermediate pro- duct. The acid is very stable towards sulphuric acid, merely passing into its internal anhydride with loss of water; more strongly heated it gives a little carbon dioxide and is sulphonated. The sulphuric acid it is also said to form an infinite additive compound,  $C_6H_4O_4 + H_2SO_4$  (ogewerf and van Dorp, D. R. P. 21352). Thielis has prepared a "phthalic acid"  $(OH)_2 \cdot C_6H_3 \cdot AsO(OH)_2$  (Ber. 1885, 18, 2687). The constitution of the acid has been determined by Nölting (Ber. 1885, 18, 2687) by oxidising the three xylenes with per- manganate obtained excellent yields of the phthalic acids. As meta-xylene forms three isomeric nitro-xylenes, xylenidines and xylenols, o- two, and para- only one each of these derivatives, therefore iso-phthalic acid has positions 1, 3, ordinary phthalic 1, 2, and tera- phthalic 1, 4, for the carboxyl groups.

Phthalic anhydride is formed (1) by distilla- tion of the acid, (2) by warming the acid with phosgene (Laurent, Marignac), (3) by reaction of lead nitrate and phthalyl chloride (Schwicz, Ber. 1884, 17, 1283), (4) by heating valonic acid—itself an oxidation product of naphthalene—to 200°, (5) dissolving the acid in nitrobenzene, anisole, or veratrole, containing  $P_2O_5$  (Z. chim. ital. 30, ii. 361), (6) shaking a solution of sodium phthalate with two molecules of sulphuric acid (Gazz. chim. ital. 26, ii. 482). These methods are represented ultimately by the equation—



Phthalic acid is the only one of the three isomeric acids which gives in this way an anhydride. A novel method of preparation is given by Denham (Chem. Soc. Trans. B, 95, 1235) from the interaction of sulphuric acid on the sodium salt—



The anhydride exists as long, tough needles, m.p. 128°, b.p. 284°; it is very sparingly soluble in cold, more readily so in hot, water, being usually reconverted into phthalic acid; in alcohol and ether it is readily soluble, and gives in alkalies forming phthalates. With ammonia it gives phthalimide (see below); with alcoholic ammonia phthalamic acid,

$\text{C}_6\text{H}_4(\text{CONH}_2)\text{COOH}$ , m.p. 149°; and with aqueous ammonia it yields ammonium phthalamate  $\text{C}_6\text{H}_4(\text{CONH}_2)\text{COONH}_4$ , which on heating is transformed into phthalimide (see later).

Fusion of phthalic anhydride with lime produces benzene and diphenyl (Annalen, 1879, 196, 48); with zinc dust it gives biphtalyl,  $\text{C}_{16}\text{H}_8\text{O}_4$ , and with zinc dust and methyl iodide yields dimethyl phthalide  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array} \text{O}$ .

In contact with alkaline hydrogen peroxide it reacts with formation of monophthalic acid,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{OH}$  and the external anhydride of this. Three molecules of phthalic anhydride combine with 2 molecules of  $\text{SbCl}_5$  to form a crystalline compound.

The usual method of purification of small quantities of phthalic anhydride is that of fusion with about twice the weight of resorcinol in presence of a drop of concentrated sulphuric acid. In this way fluorescein is produced (v. *infra*), and the reddish-brown product, when dissolved in dilute caustic soda and poured into a large volume of water, yields a magnificent green fluorescent solution. This reaction is shown by all the phthalic acids of the benzene series, and is the basis of the formation of a variety of coloured solutions, but it is not shown by the meta- or para-dicarboxylic acids. Succinic anhydride does not undergo this reaction.

A method of purification of phthalic anhydride from a mixture of impurities is given by J. Amer. Chem. Soc. 1907, 29, 230). It consists in the careful sublimation of the anhydride and subsequent titration with standardised caustic soda.

#### TECHNICAL MANUFACTURE.

Owing to the extensive use of phthalic anhydride in the manufacture of synthetic indigo (*q.v.*) and the pyronine and triphenylmethane class of dye-stuffs, a cheap technical process for its preparation in large quantities was essential, and this has been achieved in the various patents of the Badische Anilin u. Soda Fabrik (*cf.* D. R. P. March 31st, 1896, 91202; Eng. Pat. 18221; August 17th, 1896; Frdl. 1894-1897, 164), which are based upon the observation that naphthalene is readily oxidised by concentrated sulphuric acid containing mercuric sulphate, its oxide, or the metal itself, which acts as a catalyst, and that the sulphur dioxide formed by the reduction of the mineral acid is reconverted into sulphuric acid by absorption of oxygen from the air, the whole process being practically continuous.

In the English patent the quantities given are as follows:—

100 kilograms	naphthalene
1500 "	sulphuric acid (100 p.c. $\text{H}_2\text{SO}_4$ )
50 "	mercuric sulphate.

In place of naphthalene,  $\beta$ -naphthol, naphthionic acid, or phenanthrene may be used. The mercury sulphate remains behind as residue in the retort and is used over and over again.

It should be borne in mind that a too vigorous oxidation will destroy the phthalic acid as soon as formed, and therefore the preparation should be conducted within well-defined limits of temperature—about 270°–300°.

A detailed account of the exact conditions employed, with a description of the manufacturing plant, is given below.

In a vertical cylinder fitted with a mechanical stirrer, the following substances are mixed, and agitated for three hours until the naphthalene is completely dissolved:—

3675 kilos. sulphuric acid 66°Bé.  
1050 „ oleum (23 p.c. SO<sub>3</sub> content).  
350 „ naphthalene.

The solution (A) so prepared is stored in a reservoir until required.

The oxidation vessel consists of an iron pan, built round with bricks and carefully heated by means of gas jets. The pan possesses a removable lid, has a flat bottom, a diameter of 6 feet and is 2 feet deep; a wide tube for leading off the vapours is provided, and through the top passes a shaft connected with a two-arm stirrer, worked mechanically, which just scrapes the bottom of the pan; also several iron marbles are allowed to rotate on the pan bottom to attract charred matter, and a pressure gauge is inserted on the lid.

The phthalic anhydride sublimes simultaneously with quantities of sulphuric acid which distils over, and these vapours are conducted through a short pipe, 8 inches in diameter, into the condenser, which consists of three concentric lead cylinders fixed one within the other at a distance of about a foot; two of these communicate with one another through the bottom and open into the third, which is surrounded by an outer condenser, through which water is circulated. The third of these cylinders is again connected with a reservoir into which the condensed sulphuric acid overflows. On the lid of the closed condensers is a vacuum arrangement which conducts off the sulphur dioxide as soon as formed, to an absorption apparatus.

At the beginning of the operation the oxidation pan, containing 120 kilos. of sulphuric acid-monohydrate and 4 kilos. of mercury, is heated for 1½ hours very gently until all the monohydrate distils over, the stirring apparatus being worked during this operation. The prepared solution (A) is now admitted into the pan from the reservoir above, in portions of 22 litres, the temperature being regulated that the reaction should last for 13–17 minutes. The end of each operation is observed by the increased noise of the rotating marbles on the bottom of the pan, and a further measured lot of 22 litres is then run in.

The process is continued until the pan contains so much charred matter that it is advisable to clean it. The progress of the anhydride formation is controlled by gas analysis, the amount of CO<sub>2</sub> evolved being determined from time to time. When the CO<sub>2</sub> content reaches 0.6–0.8 p.c. the addition of naphthalene solution (A) is discontinued, and the mixture is stirred three times the volume of (A) is admitted and distilled away, after which the vessel is again ready for 2 or 3 days' continuous working. Should the CO<sub>2</sub> gas-content reach 1 p.c., the work is interrupted for a complete cleaning of the pan; the pan is heated until perfectly dry, the charred matter is chipped from the interior.

To separate the sulphuric acid and phthalic

anhydride which together collect in the condenser, the clear sulphuric is first decanted, and then the crude phthalic anhydride is further separated centrifugally and washed free from acid. The product is dried and purified by resublimation in a pan mechanically stirred, and heated over a coke fire. A large cylindrical vessel serves as condenser. The cost of this process, as worked in Germany, is about one mark per kilogramme of phthalic anhydride.

Other less well-known methods which may have some technical value for the preparation of phthalic acid are given below.

O. Imray, of the Basle Chemical Works, took out an English patent, No. 15527, on July 31, 1901, for the heating of naphthols in presence of a very slight excess of alkali, with metallic oxides or peroxides, such as copper and iron oxides or barium, lead, or manganese peroxide, to a temperature of about 240°–260°C. for 8 hours in oxygen gas under pressure. Phthalic and some benzoic acid are formed, together with a few intermediate products (see Ber. 1888, 21, 1016). Not only naphthols, but also nitro-naphthalenes, naphthylamines, and naphthalene sulphonics acids may be used (cf. D. R. PP. 136410, 138790, 139956, 140999; Frdl. 1902–1904, 112–115).

Many patents have been granted for the use of salts of rare earths as catalysts in the oxidation of naphthalene by means of sulphuric acid. The nitrates, oxalates, carbonates, oxyhydrates, sulphates of cerium, lanthanum, neodymium, praseodymium, ytterbium, have all been used as substitutes for the mercury in the original German patent, No. 91202 (see above). A mixture of—

25 grms. naphthalene  
375 „ concentrated sulphuric acid  
15 „ oxide of rare earths

evolves gas gently at 100° and at 200° a vigorous evolution of SO<sub>2</sub> and CO<sub>2</sub> begins and continues briskly until the thermometer registers 270°. Pure white crystals of phthalic anhydride sublime over into the receiver (D. R. PP. 142144, 149677, 152063, 158609). It is claimed that the use of rare earths as a substitute for mercury salts is more economical, as they can always be recovered from the residue in the retort, although the yield is not quite so good as with the use of mercury. A process for the oxidation of naphthalene by electrolysis of a solution of 20 p.c. sulphuric acid and 2 p.c. cerium sulphate is also described (Frdl. 1902–1904, 105–107; D. R. P. 152063).

The observation that naphthalene is soluble in boiling water has been utilised by Procházka (Ber. 1897, 30, 3108) for its oxidation to phthalic acid by means of hot permanganate. Almost theoretical results are obtained, phthalonic acid being produced as an intermediate stage. The reduction of permanganate is very rapid, and the best results are obtained when a large excess of naphthalene is employed, the unchanged hydrocarbon being easily recovered; 100 grms. commercial permanganate yield 17 grms. phthalic acid, the theoretical yield being 19 grms.

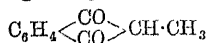
The Basler Chem. Fabrik have taken out a patent (D. R. P. 136410; Frdl. 1900–1902, 1301) for the manufacture of phthalic acid together with benzoic acid from *o*-nitro-naphthalene

and nitrophenols by the action of alkalis under pressure and in a dilution medium such as common salt.

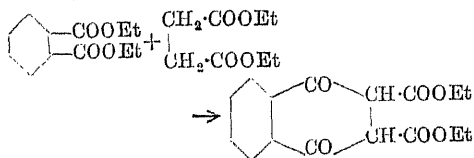
**Esters of phthalic acid** with most of the known alcohols have been prepared in the usual way. The dimethyl ester distils at 280°/734 mm.; diethyl ester at 295°; diphenyl ester melts at 73°; benzyl acid ester has m.p. 106°-107°, affording a good characterisation of benzyl alcohol; cyclohexanol acid ester, m.p. 99°, neutral ester m.p. 66°. Various esters of phthalic acid are used as solvents for resins, e.g. copal resin, which need not be melted to be dissolved (Hesse, D. R. P. 227667).

Pickard has accomplished the resolution of various complex alcohols into their optically active components by making the acid-ester by simple fusion with phthalic anhydride and combining this with active bases (Chem. Soc. Trans. 1907, 91, 1974).

Ethyl phthalate reacts with ethyl acetate and sodium to form ethyl diketohydrindene carboxylate; and with ethyl propionate and sodium, yielding methyl diketohydrindene—



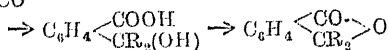
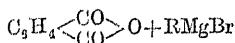
If ethyl succinate be substituted for ethyl propionate, ethyl dihydronaphthraquinone dicarboxylate is formed.



#### Derivatives and Condensation Products of Phthalic Anhydride.

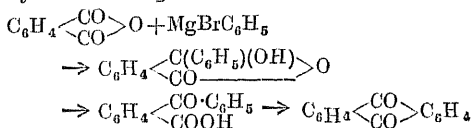
The extraordinary reactivity of the anhydride accounts for the great number of important derivatives which have been prepared. First among these should be mentioned *phthalyl chloride*  $\text{C}_6\text{H}_4 \begin{array}{c} \text{COCl} \\ \diagup \quad \diagdown \\ \text{COCl} \end{array}$ , obtained by the action of phosphorus pentachloride. It is a liquid of b.p. 275°/726 mm., solidifying at 0°C. From this, by the action of ethyl alcohol, is obtained the ether,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO(OEt)} \\ \diagup \quad \diagdown \\ \text{CO(OEt)} \end{array}$ , while it also condenses with ketones or with ethyl sodioacetate (Fischer and Koch, Ber. 16, 651; Bülow and Koch, Ber. 1904, 37, 577; 1905, 38, 474). Reduction of phthalyl chloride with zinc and hydrochloric acid produces the important derivative *phthalide*  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , m.p. 73° (v. LACTONES), and with acetic acid and sodium amalgam the phthalyl alcohol,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2\text{OH} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{OH} \end{array}$ .

Grignard's reagents act on phthalic anhydride, forming the dialkyl and trialkyl esters, of which a large variety have been prepared:—



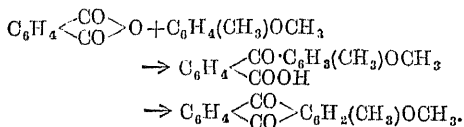
(cf. Bauer, Ber. 1904, 37, 735; 1905, 38, 240;

Arch. Pharm. 247, 220). Pickles and Weizmann (Chem. Soc. Proc. 1904, 20, 201) have prepared *mono-aryl hy*... by this means, which give by... keto acids; anthraquinone has thus been prepared by the following series of reactions:—

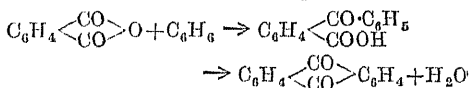


Simonis and Arand (Ber. 1909, 42, 3721) have succeeded in obtaining acyl benzoic acids by the interaction of Grignard reagents and phthalic acid itself, in addition to the dialkyl phthalides just described, e.g. using excess of magnesium ethyl bromide he isolated *o*-carboxy-phenyl ethyl ketone, m.p. 97°,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{COC}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{COOH} \end{array}$ .

Phthalic anhydride condenses with the cresols or their methyl ethers in presence of boric acid or aluminium chloride (cf. phthalein reaction with phenol):

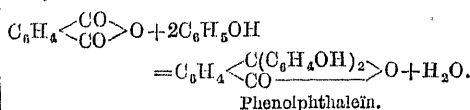


Sulphuric acid effects the closing of the ring in the condensation product, giving oxy-methyl anthraquinones and their methyl derivatives (v. METHYL ANTHRACENE; cf. Bentley, Gardner, and Weizmann, Chem. Soc. Trans. 1907, 91, 1626; Lambrecht, Ber. 1909, 42, 3591). The simplest case of the above condensation was worked out by Friedel and Crafts, who condensed phthalic anhydride and benzene in presence of aluminium chloride, with the ultimate formation of anthraquinone:—



(V. ANTHRAQUINONE, also Friedel and Crafts, Ann. Chim. Phys. [vi.] 14, 446; Heller, D. R. P. 193961.)

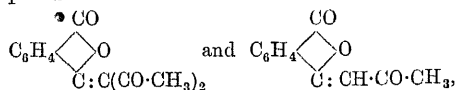
Phthalic anhydride condenses with phenols in presence of a catalyst like zinc chloride or sulphuric acid, yielding a class of colouring matters known as the phthaleins, which are fully dealt with in the article on TRIPHENYLMETHANE COLOURING MATTERS. The simplest member of the series, phenolphthalein, is prepared by condensing 2 molecules of pheno (Baeyer, Ber. 1874, 7, 968)—



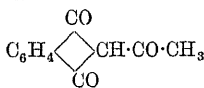
When resorcinol is substituted for phenol in this condensation, the product is the beautiful green fluorescein acid, the sodium salt of which is known in commerce as the dyestuff uranine—



it with acetyl acetone, and obtained the products—



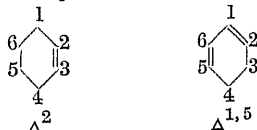
the second of which readily passes into  $\beta$ -acetyl diketo-hydrindene—



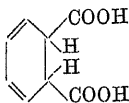
(cf. also Eibner, Ber. 1906, 39, 2202).

### THE HYDROPHTHALIC ACIDS.

The classical work associated with the name of von Baeyer on the reduction of the phthalic acids has done much to extend our knowledge of valency, and especially of the constitution of the benzene ring. His researches (Annalen, 1873, 166, 346; 1890, 258, 214; 1892, 269, 154) enunciate the general rule, that entrance of hydrogen atoms into the molecule of the acid, always takes place by addition to the  $\alpha$ -carbon atoms, i.e. those which are adjacent to carboxyl groups. For example, adopting the special nomenclature for the hydrobenzenes, namely—

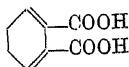


then the reduction of ortho-phthalic acid with sodium amalgam in weak acetic acid solution, gave rise to the *trans*- $\Delta^{3,5}$ -dihydrophthalic acid



which melts at 210°. This is also prepared by electrolysis of phthalic acid in hot 15 p.c. aqueous sulphuric acid (Mettler, Ber. 1906, 39, 2941). The *cis*-form is only obtained by acting on this with acetic anhydride for 7 minutes, when the *cis*-anhydride, m.p. 100°, is formed, which on boiling with water yields the *cis*-acid, m.p. 175°; prolonged boiling converts the *cis*- into *trans*-form. The above  $\Delta^{3,5}$  acid is what is known as a  $\beta\gamma$  doubly unsaturated acid, the double linkings being both attached to  $\beta\gamma$  carbon atoms with reference to the carboxyl groups. This type of acid readily undergoes inversion by digesting with alkalis such as caustic soda, due to the shifting of the double bonds to the  $\alpha\beta$  position in each case, so that the compound

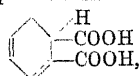
$\Delta^{2,6}$ -dihydrophthalic acid



is obtained. This acid is exclusively formed when the reduction of phthalic acid with sodium amalgam is carried out in alkaline solution. It melts at 215°, and its anhydride, formed by

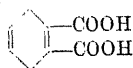
the action of acetyl chloride, melts at 84°. Benzoic acid may be obtained from this  $\Delta^{2,6}$ -acid on oxidation. It is not affected by boiling with aqueous caustic soda, but very concentrated alcoholic potash produces the

$\Delta^{2,4}$ -Dihydrophthalic Acid



which melts at 180°, and which is also obtained indirectly from the dihydrobromide of  $\Delta^{2,6}$  dihydrophthalic acid and methyl alcoholic potash. When this  $\Delta^{2,4}$ -acid is boiled for 6 minutes with acetic anhydride, the anhydride of a new acid,

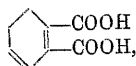
$\Delta^{1,4}$ -Dihydrophthalic Acid



is formed, and on boiling with boiling water the above acid, m.p. 153°. Boiling caustic soda converts it into the  $\Delta^{2,4}$  and  $\Delta^{2,6}$  isomerides. It may be oxidised back again into phthalic acid. The anhydride of the acid melts at 133°.

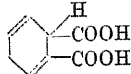
Abati and Bernardinis (Chem. Zentr. 1905, i. 1318) have isolated the two remaining dihydrophthalic acids by a careful scheme for separating the initial reduction products obtained as described by Baeyer. These are the—

$\Delta^{1,3}$ -Dihydrophthalic Acid



the anhydride of which melts at 59°–60°, and also the

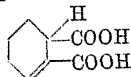
$\Delta^{2,5}$ -Dihydrophthalic Acid,



which is obtained by heating the  $\Delta^{1,3}$ -acid to 230° in a closed tube; also by the intermediate shifting of the double linking in the  $\Delta^{3,5}$ -acid by means of caustic soda. Its anhydride melts at 73° (cf. also Abati, Gaz. chim. ital. 38, i. 152).

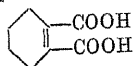
The Tetrahydrides are five in number. On reducing a boiling solution of sodium phthalate with sodium amalgam,

$\Delta^2$ -Tetrahydrophthalic Acid



is formed, m.p. 215°; the anhydride melts at 79°, and is made by heating the acid. When this acid is heated for a considerable time at its melting-point, the anhydride of

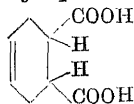
$\Delta^1$ -Tetrahydrophthalic Acid



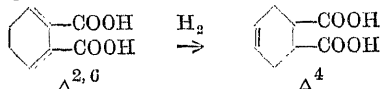
is produced, which on boiling with water gives rise to the above  $\Delta^1$ -acid, m.p. 120°. The anhydride melts at 74°. This is also prepared by

by distilling the tetrahydride of pyromellitic acid. It changes back into the  $\Delta^2$ -acid with concentrated potash, and permanganate oxidises it to adipic acid

*Trans- $\Delta^4$ -tetrahydrophthalic Acid*

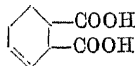


is formed, together with  $\Delta^2$ -acid, by reducing the  $\Delta^{2,6}$  dihydride in boiling water with sodium amalgam, that is—



(Cf. Thiele, Annalen, 1899, 306, 125.) This  $\Delta^4$ -acid melts at  $218^\circ$ ; its *anhydride*, made by the action of acetyl chloride, melts at  $140^\circ$ , and the *methyl ester* melts at  $40^\circ$ . The acid changes on heating into the *cis-form*, which is also obtained by reducing the  $\Delta^{2,4}$ -acid at  $0^\circ$  with sodium amalgam. This *cis- $\Delta^4$* -acid melts at  $174^\circ$ , and its *anhydride* at  $58^\circ$ .

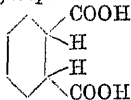
The remaining isomeride—  
 *$\Delta^3$ -Tetrahydrophthalic Acid*



is described by Abati and Vergari (Gazz. chim. ital. 1909, 39, ii. 142). Its *anhydride* melts at  $70^\circ$ – $71^\circ$ .

Both the di- and tetra-hydrophthalic acids are unstable towards permanganate and with milder oxidising agents may be oxidised back to phthalic acid. They form, as a rule, additive compounds with bromine or hydribromic acid, and yield on reduction hexahydrophthalic acid (cf. also Graebe and Born, Annalen, 1867, 142, 330; Astie, Annalen, 258, 187). The physical properties of all these acids have been carefully measured by Abati and his collaborators (Gazz. chim. ital. 39, ii. 142; Chem. Zentr. 1907, i. 886).

*Trans-hexahydrophthalic Acid*



is prepared by reducing all the lower hydrides or their halogen additive compounds, either with sodium amalgam or zinc dust and acetic acid. It melts at  $221^\circ$ , and is not oxidised by cold permanganate. The *anhydride* melts at  $140^\circ$ , and the *methyl ester* at  $33^\circ$ . When slowly reduced, it yields the *anhydride of cis-hexahydrophthalic acid*, from which the free acid is obtained by boiling with water. The acid melts at  $192^\circ$ , and the *anhydride* at  $32^\circ$ .

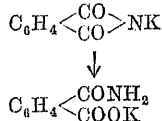
NITROGEN DERIVATIVES.

Phthalimide  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} NH$  is formed by the action of ammonia gas on molten phthalic anhydride, and is a most important stage in the manufacturing process of synthetic indigo. The method, due to Kuhara, is a quantitative

one. Dry ammonia gas compressed in cylinders is used, and is passed into the phthalic anhydride until it ceases to be absorbed, the process occupying in all about 18 hours. The chief condition is that at the end of the operation, when complete transformation of anhydride into imide has been effected, the mass should remain in the molten state; the anhydride melts at  $128^\circ$  and the imide at  $228^\circ$ , hence during the progress of the operation the temperature should be maintained  $1^\circ$  above the latter. The molten product is run off and allowed to cool and crystallised in open pans; 650 kilos. of anhydride yield 635 kilos. of phthalimide.

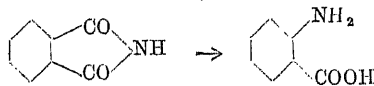
Phthalimide may also be prepared by heating phthalic anhydride with urea (Dunlap), or with aliphatic nitriles (Matthews, J. Amer. Chem. Soc. 1896, 18, 680; 1898, 20, 654), or with formamide, acetamide, and other amides, acetanilide, and similar compounds. It exists as colourless plates, m.p.  $228^\circ$ , and may be sublimed.

*Reactions.*—Amyl alcohol and sodium reduce phthalimide to *o*-methyl benzylamine (Bamberger, Ber. 1888, 21, 1888). Distilled with lime, it loses water and carbon dioxide, yielding benzonitrile (Reese, Annalen, 1887, 242, 5). With alcoholic potash it forms a potassium derivative,

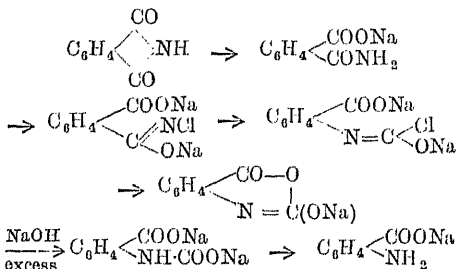


which on boiling with water is converted into potassium phthalamate.

From the point of view of indigo its most important reaction is that discovered by Hoogewerff and van Dorp (D. R. P. 55988), with alkaline KBr at  $80^\circ$ , when it is transformed into *o*-aminobenzoic acid, or anthranilic acid—

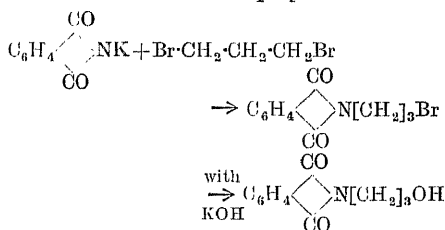


Mohr (J. pr. Chem. [ii.] 80, 1; D. R. P. 127138, 139218; Frdl. 1902–1904, 118–120) has modified this by using NaOCl, and states that sodium isatoic acid anhydride is probably formed as an intermediate compound, which excess of caustic soda converts into sodium anthranilate—



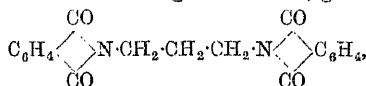
Phthalimide forms a potassium derivative exactly as does malonic ester, in which also the metallic radicle may be substituted for alkyl by contact with halogen compounds (see résumé by Sørensen, Zeitsch. physikal. Chem. 44, 448; Chem. Zentr. 1905, ii. 401; cf. also Bull.

Soc. chim. 33, 1042). Gabriel describes an interesting example of this use of potassium phthalimide with dibromopropane—



(Ber. 1905, 38, 2389).

Two molecules of phthalimide may also combine with the halogen derivative, giving



and this on hydrolysis with mineral acids yields trimethylene diamine and 2 molecules of phthalic acid, thus providing an excellent general method for the preparation of diamines.

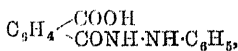
Various mercaptan derivatives of phthalimide have been prepared by Manasse (Ber. 1902, 35, 1367).

The German patent No. 139553 describes the preparation of *phthal-chlorimide* by leading chlorine into an aqueous suspension of phthalimide.

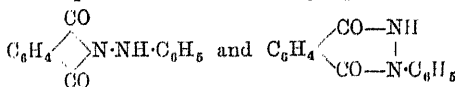
A 40 p.c. solution of formaldehyde gives with phthalimide a methyl phthalimide of m.p. 132° (Breslau and Pictet, Ber. 1907, 40, 3784). Various Grignard reagents have been tried with success upon phthalimide (*cf.* Béis, Compt. rend. 138, 987; Sachs and Ludwig, Ber. 1904, 37, 385). With tin and hydrochloric acid it is reduced to phthalimidine  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$  (Graebe, Ber. 1884, 17, 2598; Annalen, 1888, 247291).

Phthalyl hydrazide  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ | \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$  is made

from the anhydride and hydrazine (Curtius, J. pr. Chem. [ii.] 51, 376). The phenyl hydrazine derivatives exists in two forms; the first product of the condensation is probably a simple additive compound—



which splits off water in two ways, giving—



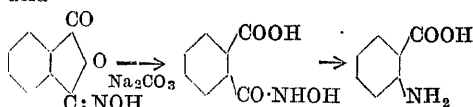
$\alpha$  Phthalyl phenylhydrazine, m.p. 179°.  $\beta$  form.

(Dunlap, J. Amer. Chem. Soc. 1905, 27, 1091).

Phthalyl semicarbazide melts at 262°.

Phthalylhydroxylamine. Hydroxylamine condenses with phthalic anhydride in aqueous dilute alcoholic solution or in caustic soda, with formation of phthalylhydroxylamine, m.p. 204°–206° in good yields (Basler Chemische Fabrik, D. R. PP. 130680, 130681). Treatment of the hydrochloride of this with sodium carbonate, and subsequent action of caustic

soda, leads to the formation of anthranilic acid—



(D. R. P. 136788; Frdl. 1902–1904, 117).

Phthalanil  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ , m.p. 205°.

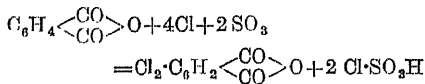
is formed by heating 1 molecule of sodium phthalate and 2 molecules of aniline hydrochloride in a closed tube for 6 hours at 200° (J. Amer. Chem. Soc. 1903, 25, 612).

Phthalonitrile  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CN} \\ \diagup \quad \diagdown \\ \text{CN} \end{smallmatrix}$  is obtained from 2-aminobenzonitrile by conversion of the  $\text{NH}_2$  group into CN (Pinnow and Sämann, Ber. 1896, 29, 630); and from *o*-cyanobenzaldoxim by dehydration in contact with acetic anhydride (Posner, Ber. 1897, 30, 1693). It forms odourless needles, m.p. 142°, distils without decomposition, and is volatile in steam. It is transformed into phthalic acid on hydrolysis with concentrated hydrochloric acid.

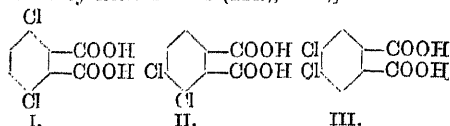
Seminitrile of Phthalic acid  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CN} \\ \diagup \quad \diagdown \\ \text{COOH} \end{smallmatrix}$  (*o*-cyanobenzic acid) is prepared from anthranilic acid by the Sandmeyer reaction (Ber. 1885, 18, 1499); by the action of  $\text{NH}_3$  upon phthalyl chloride (Hoogewerff and van Dorp, Rec. trav. chim. 11, 91; *cf.* Kuhara, Amer. Chem. J. 3, 26; Auger, Ann. Chim. Phys. [vi.] 22, 289); and from benzaldehydeoxime-carboxylic acid by contact with acetic anhydride. It exists as needles melting at 180°–190° and changing simultaneously into phthalimide. Heating with water produces acid ammonium phthalate. The methyl ester melts at 51°, and the ethyl ester at 70°.

#### SUBSTITUTED PHTHALIC ACIDS.

Many *chloro*, *bromo*, *nitro*, *sulpho* substituted phthalic acids are known, and references to these are frequent in Beilstein's Handbuch der Organischen Chemie, vol. ii. and its supplement; also Frdl. 1887–1890, 93; Villiger, Ber. 1909, 42, 3529. When phthalic anhydride, dissolved in fuming sulphuric acid, is treated with chlorine in presence of a little iodine (Juvalta, D. R. P. 50177), the following reaction occurs:—



Separation of the products is possible owing to a difference in solubility of the zinc salts, by a recrystallisation of which three isomerides are separated. The chief product is 3:6-dichloro phthalic acid (I.), smaller quantities of 3:4 (II.) and very little of 4:5 (III.), being isolated—

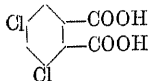




The 3:6 acid has m.p. 253°–258°; and its anhydride, m.p. 339°.

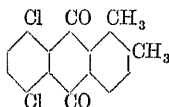
These acids are more soluble in water and ether than ordinary phthalic acid, and the anhydrides can be distilled (cf. also Graebe, Ber. 1900, 33, 2019).

A fourth isomeride is described by Crossley and Le Sueur (Chem. Soc. Trans. 1906, 81, 1533),

viz. the 3:5-dichlorophthalic acid 

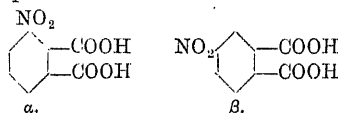
(cf. also Claus, Ber. 18, 1370; 19, 3175; J. pr. Chem. [ii.] 43, 253, 582; Le Royer, Annalen, 1887, 238, 350).

3:6-dichlorophthalic anhydride, which is now a commercial product, has been condensed with the three xylenes and the closing of the ring effected, with formation of dichloro- (Harrop, Norris and trans. 1909, 95, 1312)—



Of the four possible dibromophthalic acids only the *para* (3:6-), m.p. 135°, is at present made, the yield being 30 p.c.; 100 grams of dibromonaphthalene is strongly heated for 2 hours with 2 litres of nitric acid (sp.gr. 1.4); first a nitrated product is obtained, and then on evaporation of the mother liquors to one-third the volume, white crystals of the 3:6-dibromophthalic acid appear (Severin, Chem. Zentr. 1907, i, 1119).

*Nitro-phthalic acid.* Holleman (Chem. Zentr. 1908, ii, 2011) has studied quantitatively the action of concentrated nitric acid on phthalic acid at 30°, and has found that the product contains 49.5 p.c. of the  $\alpha$ - and 50.5 p.c. of the  $\beta$ -nitrophthalic acid—

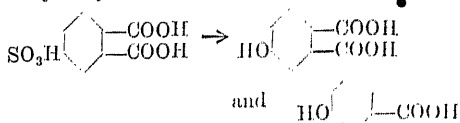


*Sulpho-phthalic acids.* The Badische Anilin und Soda Fabrik, has obtained an English patent (J. Y. Johnson, No. 18221, August 17, 1896) for the preparation of a disulphonic acid. 100 kilos. of naphthalene is dissolved in 300 kilos. of fuming sulphuric acid (23 p.c. SO<sub>3</sub>) and mixed with 1200 kilos. concentrated sulphuric acid (95 p.c.). The mass is heated for 10 hours at about 250°; a certain amount of phthalic acid distils over during the reaction. The product is neutralised with calcium or barium carbonate and worked up in the usual way. The new *disulphonic acid* of phthalic acid may be separated from water in crystalline nodules in the form of its barium salt.

If the temperature is maintained at about 220°, a *monosulphonate* of phthalic acid is obtained.

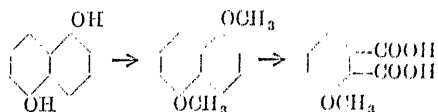
*Hydroxy-phthalic acids.* Bentley and Weizmann (Chem. Soc. Trans. 1907, 91, 98) have sulphonated phthalic anhydride with fuming sulphuric acid (73 p.c. SO<sub>3</sub>) at 200° and fused the products with caustic soda, obtaining in this

way 4-hydroxy-phthalic acid, and as by-product *m*-hydroxybenzoic acid—

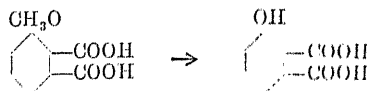


acid melts at 204°–205°, its m.p. 173°; the methoxy acid at 98°.

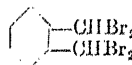
The same authors, with Miss Rona Robinson (Chem. Soc. Trans. 1907, 91, 104), prepared 1:5-di-methoxy-naphthalene and oxidised this with permanganate, obtaining 3-methoxy-phthalic acid, m.p. 173°, the anhydride of which melts at 160°—



Fusion of the methoxy acid with caustic potash gives rise to 3-hydroxy-phthalic acid, m.p. 150°—

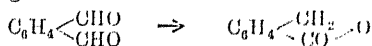


*Phthalaldehyde* C<sub>6</sub>H<sub>4</sub><CHO. When *o*-xylene is brominated it yields the tetrabromide

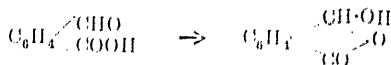


If 400 grams of this bromide are heated with 360 grams of finely powdered crystalline potassium oxalate in an oil-bath for 40 hours, in contact with 2½ litres of water and 2½ litres of 95 p.c. ethyl alcohol, a clear yellow solution results, with evolution of some carbon monoxide and dioxide. After distilling off 2 litres of alcohol, which is used again subsequently, 700 grams of crystalline sodium phosphate are added, and the mass is subjected to distillation in steam, which drives over the phthalic aldehyde. The product is readily soluble in water, and therefore the distillate is extracted several times with acetic ester, which dissolves out the aldehyde, a 90 p.c. yield being obtained in the form of yellow needles, m.p. 56° (Thiele and Günther, Annalen, 1906, 347, 106).

Strong alkali converts phthalaldehyde into phthalide, which appears to be an intramolecular change into a more stable isomeride—



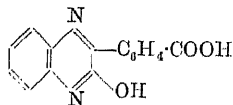
It is interesting to compare this with the 'lactone tautomerism' of aldehyde phthalic acid and hydroxy phthalide, which can react in either form—



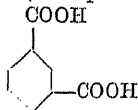
Phthalaldehyde condenses readily with a large number of substances by virtue of its two —CHO groupings; e.g. with acetone it

$$\begin{aligned} \text{C}_6\text{H}_4 < \begin{array}{c} \text{CHO} \\ \text{CHO} \end{array} + \text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \\ = \text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ \text{CO} \end{array} > \text{CH} \cdot \text{CO} \cdot \text{CH}_3 + \text{H}_2\text{O} \end{aligned}$$

Phthalonic acid takes part in numerous reactions, principally those involving the keto group: *e.g.* it condenses with *o*-phenylene diamine (Gazz. chim. ital. 1904, 34, i. 493), giving the compound—

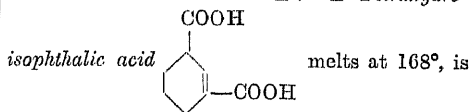

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{COOH} \\ \diagdown \quad \diagup \\ \text{COOH} \end{array} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CHO} \\ \diagdown \quad \diagup \\ \text{COOH} \end{array} + \text{CO}_2$$

**isoPhthalic acid** (meta-phthalic acid)

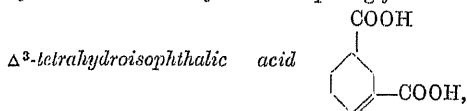


It forms a *hydrazide*, m.p. 220°, by heating with hydrazine hydrate in absolute alcohol (Davids, J. pr. Chem. [ii.] 54, 74), and also an *azide*,  $C_6H_4(CON_3)_2$ .

All the four possible *tetrahydro* acids have been isolated. *iso*-Phthalic acid on reduction with sodium amalgam yields two acids,  $\Delta^2$  and the *cis*-form of  $\Delta^4$ .  $\Delta^2$ -*Tetrahydro*-

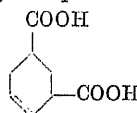


very soluble in water, and its anhydride melts at 78°. By the agency of caustic potash or hydrochloric acid it yields the sparingly soluble



m.p. 244°, which gives, with acetic anhydride, the anhydride of  $\Delta^2$ -acid, m.p. 78°.

*Cis- $\Delta^4$ -tetrahydroisophthalic acid*

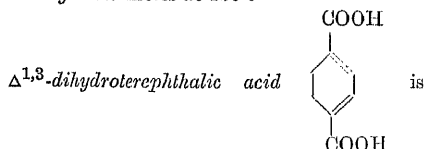


is isolated from the original reduction product, as stated above. It melts at 165°, is very soluble in water, and is easily converted into the *trans*-acid with concentrated hydrochloric acid. This trans-form is sparingly soluble, and melts at 227°.

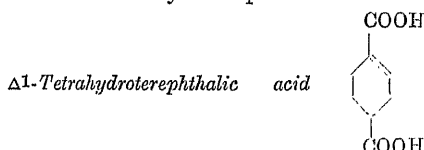
*Cis-* and *trans*-hexahydroisophthalic acids, m.p. 163° and 148° respectively, were obtained synthetically by Perkin and Prentice (Chem. Soc. Trans. 1891, 59, 808; *cf.*, however, Perkin and Goodwin, Chem. Soc. Trans. 1905, 87, 843), who condensed trimethylene bromide with sodio-methylene-malonate ester—



with sodium amalgam in alkaline solution. The methyl ester melts at 130°.

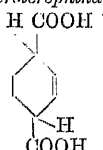


prepared indirectly from the dibromide of  $\Delta^2$ -tetrahydroterephthalic acid by the action of methylmagnesium iodide. Its methyl ester melts at 85°. In accordance with Thiele's view of the reduction of conjugated double linkings, it reduces to  $\Delta^2$ -tetrahydroterephthalic acid.



is prepared by boiling 1 part of terephthalic acid in caustic soda for 40 hours, and gradually adding 100 parts of sodium amalgam (4 p.c.). It melts above 300°; the methyl ester melts at 39° (Baeyer, Ber. 1886, 19, 1805; Annalen, 1888, 245, 160; 1890, 258, 32).

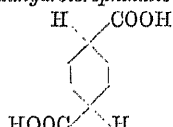
*Trans*- $\Delta^2$ -tetrahydroterephthalic acid



melts about 220°, and is obtained from the  $\Delta^{1,5}$ -dihydro acid or from the dibromo- $\Delta^{1,3}$ -acid by reduction. The methyl ester melts at 3°.

*Cis*- $\Delta^2$ -tetrahydroterephthalic acid is formed together with the *trans*-form by reducing the  $\Delta^{1,4}$ -dihydro-acid with sodium amalgam in the cold.

*Trans*-hexahydroterephthalic acid



is formed on heating the tetrahydro acids with aqueous hydriodic acid at 240°. It melts at 300°; its methyl ester melts at 71° (Baeyer, Ber. 1886, 19, 1806; Annalen, 1888, 245, 170; 1889, 251, 257). Its synthesis has been accomplished by Mackenzie and Perkin (Chem. Soc. Trans. 1892, 61, 174).

The *cis*-form, m.p. 162°, is obtained by reducing the very soluble bromo-hexahydroterephthalic acid with zinc dust and acetic acid. Its methyl ester does not crystallise.

**2:5-dichloroterephthalic acid** has been prepared by Bocchi (Gazz. chim. ital. 26, ii. 406) from the dichlorocymene by oxidation with nitric acid.

**Terephthalic aldehyde** is prepared exactly as described in the case of phthalic aldehyde (Annalen, 1906, 347, 110). It exists as for the aldehydes, m.p. 116°.

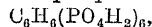
**PHTHALIC ANHYDRIDE** *v.* **PHTHALIC ACID**.

**PHTHALIDE** *v.* **LACTONES**.

**PHYCITE**. Identical with erythrol (*q.v.*).

**PHYSOSTIGMINE** *v.* **ORDEAL BEAN**; also **VEGETO ALKALOIDS**.

**PHYTIN**, *inositol phosphoric acid*



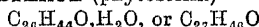
occurs in many plant seeds, usually as the calcium-magnesium salt. In bran, in the seeds of red-fir, peas, beans, pumpkin, red and yellow lupin, and in the potato and other tubers and bulbs, the greater part of the phosphorus exists in this form (Patten and Hart, Amer. Chem. J. 1904, 31, 564).

It occurs to the extent of 2 p.c. in wheat bran and 8 p.c. in rice-bran (Suzuki and others, Bull. Coll. Agric. Tokyo. 1907, 7, 495), and is prepared from the latter by extraction with 0.2% hydrochloric acid. It is purified by dialysis, washing the precipitate with water, and again with water.

magnesia (Contardi, Atti. R. Accad. Lincei. 1909, [v.] 18, i. 64). It is soluble in water and dilute alcohol; insoluble in benzene, ether, &c.; it does not crystallise (Posternak, Compt. rend. 1903, 137, 337 and 439). In plants it is associated with an enzyme, *phytase*, by which it is hydrolysed into inositol and phosphoric acid; this hydrolysis can also be brought about by dilute acids or by 20 p.c. caustic soda at 220° (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118; see also Neuberg, Biochem. Zeitsch. 1908, 9, 557; Levene, *ibid.* 1909, 16, 399; Neuberg, *ibid.* 1909, 16, 406).

The solution of the pure acid is stable and, when administered to animals by the mouth, has no ill effects (Mendel and Underhill, Amer. J. Physiol. 1906, 17, 75); 35 p.c. is absorbed by the organism, the remainder being eliminated as inorganic phosphates (Horner, Biochem. Zeit. 2, 428).

**PHYTOSTEROL** (phytosterin)



is vegetable cholesterin (Hesse, Annalen, 1872, 192, 175). It is contained in calabar beans, in the bark of *Hamamelis virginiana* (Linn.) (Grüttner, Arch. Pharm. 1898, 236, 278); in the bark of *Berberis*; in *Ergot*, in the leaves of *Eriodictyon crassifolium* (Benth.) (Power and Tutin, Pharm. Rev. 1906 24, 300); in prunas bark (Finnemore, Pharm. J. 1910, [iv.] 31, 604); in the dried rhizome and roots of the yellow jasmine (Moore, Chem. Soc. Trans. 1910, 2226), and of the *Cimicifuga racemosa* (Nutt.) (Finnemore, Pharm. J. 1910, [iv.] 31, 142); in the lichen, *Endocarpon minutum* (L.) Ach. (Hesse, J. pr. Chem. 1898, [ii.] 58, 465); in wheat germs, in the wild cherry bark, in rape oil, in cocoanut, cottonseed, and in nearly all vegetable oils, and in various lamp oils (Marcusson, J. Soc. Chem. Ind. 1901, 484). It has also been found, probably in the form of esters, in certain peaty soils (Schreiner and Shorez, Chem. News, 1912, 105, 40). See also Kerstein (Chem. Zentr. 1899, ii. 91); Mügge (Zeitschr. Nahr. Genuss. 1898, 1, 45); Schmidt and Kerstein (Arch. Pharm. [iii.] 28, 49); Matthes and Rohdich (Ber. 1908, 41, 19, 1591); Matthes and Ackermann (*ibid.* 2000); Cohen (Arch. Pharm. 1908, 246, 515,

592); Powers and Rogerson (Pharm. J. 1909, iv. 29, 7; *ibid.* 1910, [iv.] 30, 326); Sani (Chem. Zentr. 1903, i. 93); Tarbourech and Hardy (*ibid.* 1907, ii. 969); Sanders (Arch. Pharm. 1908, 246, 165); Matthes and Heintz (*ibid.* 1909, 247, 161); Klobb (Compt. rend. 1909, 149, 999); Power and Moore (Chem. Soc. Trans. 1909, 246, 1987); Dorée (*ibid.* 649); Rogerson (*ibid.* 1910, 1012); Menozzi and Moreschi (Chem. Zentr. 1910, i. 1777).

**Extraction.** The seeds, bark, or leaves are treated with ligroin, the solution is then evaporated, the residue dried between filter paper and crystallised from alcohol. From oils and fats phytosterol is obtained by saponification with alcoholic alkali and subsequent extraction with ether (Raumer, Zeitsch. angew. Chem. 1898, 24, 555; Wolf, Chem. Zeit. 1898, 22, 805; Heiduschka and Gloth, Pharm. Zentr.-h. 1909, 50, 333). Phytosterol crystallises in needles and in plates, is soluble in chloroform, but insoluble in water and in alkalis and gives the same reaction as cholesterol with chloroform and sulphuric acid. It has m.p. 132°–136°, but this, as well as its constitution, varies with the source from which it is obtained.

Windaus and Hauth have resolved the phytosterols of calabar beans into two isomers, *stigmasterol* or  $\beta$ -phytosterol,  $C_{30}H_{50}O \cdot H_2O$  or  $C_{30}H_{48}O \cdot H_2O$ , m.p. 170°;  $[\alpha]_D -45.01^\circ$  at 21° in  $CHCl_3$ , which gives a sparingly soluble bromide and an acetate, m.p. 141°, and a tetra-bromo-acetate decomposing at 211°–212°.

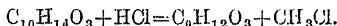
(2) *Sitosterol* or  $\alpha$ -phytosterol,  $C_{27}H_{46}O$  or  $C_{27}H_{44}O$ , m.p. 136°–137°  $[\alpha]_D -34.4^\circ$  in chloroform, which is identical with the phytosterol contained in wheat germs (Burian, Monatsh. 1897, 18, 551). It yields a readily soluble bromide, and when reduced with sodium and alcohol forms *ergosterol*,  $C_{27}H_{48}O$ , m.p. 175°, the reduction yields  $C_{27}H_{48}$ , m.p. 80°–81°. It is one of the phytosterols of m.p. about 135° consist entirely or chiefly of sitosterol (Ber. 1906, 39, 4378; *ibid.* 1907, 40, 3681; Pickard and Yates, Chem. Soc. Trans. 1908, 1929; Windaus and Welsch, Ber. 1909, 42, 612). According to Thoms (Arch. Pharm. 1897, 235, 39), the term phytosterol should be given to all unsaturated alcohols of high molecular weight, which give the characteristic cholesterol colour reactions and which owe their origin to physiological processes similar to those producing cholesterol.

**Phytosterol esters** may be obtained by heating the alcohol with 5 times its weight of the required acid or anhydride in a sealed tube on the water bath. The melting-points of some of the esters differ with the source of the phytosterol, but in all cases they are considerably higher than the corresponding cholesterol esters, and this can be used as one method of distinguishing between the two alcohols (Bömer and Winter, Zeitsch. Nahr. Genussm. 1901, 4, 865; Jaeger, Rec. trav. chim. 1907, 26, 311; Menozzi and Moreschi, *l.c.*); for other methods compare Kreis (Chem. Zeit. 1899, 23, 21); Ottolenghi (Atti. R. Accad. Lincei, 1906, [v.] 15, i. 44); Jaeger (Rec. trav. chim. 1906, 25, 334). The separation of phytosterol from cholesterol is based on the difference of the solubility of their

dibromides in a mixture of ether and glacial acetic acid (Windaus, Chem. Zeit. 1906, 30, 1011). For the detection and estimation of phytosterol in fats, see Kreis and Wolf, Chem. Zeit. 1898, 22, 805; Foerster, *ibid.* 1899, 23, 188; Wirthle, *ibid.* 250; Kreis and Rudin, *ibid.* 986; Juckenack and Hilger, Arch. Pharm. 1898, 236, 367; Ritter, Chem. Zeit. 1901, 25, 872; *ibid.* 1902, 26, Rep. 100.

For other literature on phytosterol, compare Power and Tutin (Chem. Soc. Trans. 1908, 909); Molinari and Fenaroli (Ber. 1908, 41, 2785); Heiduschka and Cloth (Chem. Zentr. 1908, ii. 1519).

**PICAMAR**  $C_{10}H_{14}O_3$  is easily obtained from wood tar; preferably from birch tar, which contains it in largest quantity. It is isolated by means of its potassium compound, which is purified by recrystallisation and decomposed by an acid; is a colourless, highly-refractive oil; b.p. 290° (corr.); and of sp.g. 1.0225 at 15°. It has a bitter taste, savouring of peppermint, and a characteristic smoky smell. It is only slightly soluble in water, but freely soluble in alcohol or acetic acid. Its most characteristic reactions are the intense blue-green colouration which it gives with ferric chloride in alcoholic solution, and the insoluble compounds it forms with the alkalis and alkaline earths. Heated with hydrochloric acid at 140° it is decomposed with formation of methyl chloride, and a crystalline product (m.p. 80°) identical in composition and properties with the substance similarly obtained by Hofmann (Ber. 11, 329) from dimethylpropylpyrogallol. This resolution of picamar may be expressed by the equation



The diaceto-derivative  $C_{10}H_{12}(C_2H_3O)_2O_3$  is easily obtained by boiling picamar (one part) with acetic anhydride (two parts) for two hours. Recrystallised from alcohol, it is obtained in long colourless needles (m.p. 83°). This is converted by the action of bromine into the dibromo-derivative  $C_{10}H_{12}Br_2(C_2H_3O)_2O_3$ . The potassium salt  $C_{10}H_{12}K_2O_3$  is easily obtained by the action of alcoholic potash to the alcoholic solution of the substance. The above results indicate that picamar is the monomethyl derivative of a higher homolog of pyrogallol, probably propylpyrogallol, and may be represented therefore by the constitutional formula:  $MeO \cdot C_6H_2(C_3H_7)(OH)_2$ .

**PICEA.** The spruce-firs: a genus of trees belonging to the conifers, the most important European member of which is the Norway Spruce (*P. excelsa*), constituting the 'White Norway', Christiania, and Danzig deals of the timber merchant, much used for flooring, joists, and rafters. The waste portions of the trunks and smaller branches are made into splints for the match manufacturer (*v.* MATCHES). Spruce wood is also used in the manufacture of paper (*v.* CELLULOSE). 'Spruce rosin' or 'frankincense' is mainly obtained from *P. excelsa*, and is used in making the better varieties of Burgundy pitch (*v.* BURGUNDY PITCH). The bark and young cones of spruce are employed as tanning materials by the Norse peasantry and an infusion of the buds in milk is used by them as a remedy for scurvy. Spruce beer is

made by adding a decoction of the green cone to the wort before fermentation. The needles of the Norway spruce, common silver fir (*Abies alba*), and some other conifers are used in the manufacture of 'pine wool' or 'forest wool,' which is spun and woven with cotton or wool to make 'hygienic flannel.' The black spruce (*P. nigra*) is chiefly found in Canada and Newfoundland. The spruce beer of America is made from the young shoots of this tree: the concentrated infusion of the buds constitutes 'Essence of Spruce.' Another species found in Canada is the White Spruce (*P. alba*).

Closely allied to *Picea* is *Tsuga*, including the Hemlock Spruce (*T. canadensis*), the bark of which is used for tanning.

Another ally is the Douglas fir (*Pseudotsuga Douglasii* and *P. macrocarpa*), which frequently rises to a height of 200 feet with a trunk measuring 8 to 10 in diameter: its timber is imported as Oregon pine.

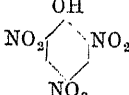
**PICENE.** Picene is contained in the least volatile portions of the residues from the rectification of petroleum. It is one of the least soluble constituents, and is best obtained by continual boiling with heavy coal-tar oils and a small quantity of strong sulphuric acid. Picene forms small colourless crystals, unaffected by ordinary solvents, the best being aniline, toluene, and the heavy coal-tar oils. Fuming sulphuric acid dissolves it with an emerald-green colouration; ordinary sulphuric acid acts in the same way. If in the latter case heat be gradually applied the colour of the solution changes from blue to greyish blue, and finally, at the boiling-point, to deep grey. If fumes conjugated sulpho acids, characterised by the beautiful blue-violet tinge of their aqueous solutions. Picene melts at 337°, and boils at 518° to 520°. Its vapour density is 9.77, the formula  $C_{22}H_{14}$  requiring 9.56. With picric acid it forms a red crystalline compound, easily decomposed by water and alcohol. It is an orange-red crystalline powder, which, on heating, is partly decomposed and partly volatilised in the form of thin needles. The latter melt at 190°, are insoluble in water and sodium bisulphite, but easily soluble in cold sulphuric acid. When strongly heated with zinc-dust, picene is oxidised, and at a lower temperature picene-oxide, a crystalline substance which resembles picene, melts at 190°, and has the formula  $C_{22}H_{12}O$ . Dibromopicene  $C_{22}H_{12}Br_2$  is obtained by brominating a solution of picene in chloroform. It forms long white needles melting at 294° to 296°.

**PICOLINE, PICOLINIC ACID** v. BONE OIL.

**PICOTITE** v. CHROMITE.

**PICRAMIC ACID** v. NITROPHENOLS.

**PICRIC ACID**  $C_6H_2(NO_2)_3OH$ , or sym-

metrical trinitrophenol,  is the

oldest artificial organic dyestuff, having been first prepared by Woulfe in 1771 by the action of strong nitric acid on indigo, who remarked upon its remarkable faculty for dyeing silk a bright yellow shade. Faussmann repeated this preparation in 1788, and investigated its acid properties, observing too its extremely bitter and nauseating taste (J. Phys. March, 1788).

Welter obtained it later as a degradation product of silk with nitric acid (Ann. chim. Phys. [i.] 29, 301), and Liebig was the first to analyse the substance, describing its salts and giving it the name carbazotic acid (Schweigger's Ann. 47, 373). Its present name of *picric acid* (Greek *πικρος*=bitter) is due to Dumas, who definitely established its composition. Laurent effected its synthesis from phenol and ascertained its chemical constitution (Ann. chim. Phys. [iii.] 3, 221).

Picric acid has been known in the literature under various names, such as yellow gall, bitter yellow, or as chrysolepinic acid, a name due to Schunck. Concerning picric acid there is an extensive bibliography, much of which is due to early workers at the beginning of last century, when the dyeing properties of this substance were considered important; only a selection of these references can be given here, along with the more recent investigations.

**Preparation.** For its laboratory preparation, one part of pure phenol is dissolved in an equal weight of concentrated sulphuric acid, and this solution added to 3 parts of nitric acid of sp.gr. 1.4 in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water bath for 2 hours. On cooling, the product solidifies to a mass of crystals, which are collected, washed, and recrystallised from hot water (Laurent, Ann. Chim. Phys. [iii.] 3, 221).

It has been obtained by the action of hot nitric acid on *indigo* (Woulfe); *aloes* (Schunck, Annalen, 39, 7; 65, 234; cf. Marchand, J. pr. Chem. [i.] 44, 91); *Botany Bay* or *Acaroid resin*, the resin of *Xanthorrhoea hastilis* (R. Br.) (Stenhouse, Chem. Soc. Mem. 3, 10; Bolley, W. J., 1858, 460; Wittstein, Dingl. J. 216, 272); *gum benzoin* (Lew, Sillman's Amer. J. [ii.] 20, 381; Kopp, Ann. chim. Phys. [iii.] 13, 233); *salicin* (Piria, Annalen, 56, 63); *saligenin*, *sabicylic acid*, *phlorizin*, *coumarin*, *balsam of Peru*, *tribromo-phenol*, the *nitrophenols*, and in general is the ultimate product of nitric acid upon most monophenolic substances (cf. Harding, Chem. Soc. Trans. 1911, 99, 1585).

Other interesting methods of formation are the following: oxidation of symmetrical trinitrobenzene with potassium ferriocyanide; the acidic nature of the nitro groups facilitates the substitution of  $-OH$  for  $H$  (Hepp, Ber. 1880, 13, 2346); aqueous sodium carbonate on picryl chloride (Ber. 1870, 3, 98; J. pr. Chem. [ii.] 1, 145).

**Manufacture.** Picric acid was formerly manufactured from acaroid resin until Laurent's discovery of the fact that it forms the end product of the nitration of phenol led to the adoption of this method for its production. At first iron filings were used at 160°–190°, was employed (Ber. 1862, 3, 585), but this was soon replaced by the pure crystallised substance which is now very largely used. To avoid the violent reaction which ensues on nitrating phenol, and to lessen the amount of resinous by-products, it is usual to sulphonate the phenol in the first instance, and then act on the resulting *phenyl sulphonic acid* with nitric acid. According to Chem. News, 37, 145), equal weights of pure crystallised phenol and sulphuric acid (sp.gr. 1.843)

are heated by steam at 100° in large iron vessels provided with mechanical stirrers, and the action is allowed to continue until a test specimen is completely soluble in water; strong nitric acid (4-5 mol. prop. to 1 mol. phenol) is then gradually added to the cooled product, which is kept well stirred until the reaction is complete. In some works the nitration is conducted in a second vessel, the phenolsulphonic acid being first diluted with twice the quantity of water, and then added gradually to the strong nitric acid contained in a stoneware vessel. In either case the picric acid is obtained as an oily, syrup-like mass, yielding large crystals on cooling; these are broken up, separated from the mother-liquor either in a filter press or centrifugal machine, washed once or twice with cold water, and then recrystallised from water containing about 1 p.c. of nitric acid, or  $\frac{1}{10}$  p.c. of sulphuric acid. In this way much of the resinous matter is removed and

purified by conversion into sodium salt, insufficient soda-lye or sodium carbonate solution (Lea, Silliman's Amer. J. [ii], 32, 182) being added in the first instance in order to bring about the separation of the remainder of the resinous matter. The filtered liquor is then rendered distinctly alkaline, whereby practically the whole of the sodium picrate is precipitated, owing to its insolubility in the alkaline liquid, and the precipitate is pressed, washed with cold water, and finally decomposed by adding an excess of sulphuric acid to its solution in boiling water—an excess of acid being employed inasmuch as picric acid is practically insoluble in a solution of sodium bisulphate.

An increased yield of picric acid is said to be obtained by heating phenol with pyrosulphuric acid at 100°-110°, and nitrating the resulting acid at 100° by the gradual addition of an accurately calculated quantity of sodium nitrate (Eisenmann and Arche, D. R. P. 51321 of May 8, 1889; Eng. Pat. 4539 of 1889).

E. de Lom de Berg has patented a method for the preparation of picric acid from crude phenol (D. R. P. 51603 of June 9, 1889; Eng. Pat. 18904 of 1889). The crude material is either fractionally sulphonated—the first fractions consisting of phenolsulphonic acid, which is subsequently nitrated—or converted wholly into sulphonic acid, and the mixture of sulphonic acids fractionally nitrated, the last fractions consisting of picric acid. The sulpho derivatives of the cresols are very soluble in water.

Köhler (D. R. P. 67074; Frdl. 1890-1894, 804) describes a process consisting of heating 100 parts phenol with 1000 parts concentrated sulphuric acid for 2 hours at 170°, which gives rise to phenol disulphonic acid; 96 parts (1 molecule) of dry powdered Chile saltpetre are now added and heated to 140°. This nitrophenol-disulphonic acid is diluted with 320 parts of water and heated to 80°-90° with 244 parts Chile saltpetre, allowing the temperature to reach 140° in about 2 hours.

Gutensohn (D. R. P. 126197; Frdl. 1900-1902, 116) proposes to obviate the explosive violence of the direct nitration of phenol by adding a solution of phenol in heated paraffin oil, or other similar mineral oil, to strong nitric acid which has also been covered by a layer of

paraffin, further quantities of this oil being added from time to time to dissolve all the phenol.

Wichardt (Fr. Pat. 345441 of 1904; Frdl. 1905-1907, 131) suggests a method of preparing picric acid without external heating, by admixture with aliphatic alcohols. A 95 p.c. yield is obtained when 20 parts phenol are mixed by constant stirring, with 100 parts nitric acid (sp.gr. 1.4) and 30 parts alcohol. Crude picric acid separates on cooling.

Wenghöffer (D. R. P. 125096; Eng. Pat. 16371 of 1900; Frdl. 1900-1902, 115) has used aniline as the initial material, converting this into sulphanilic acid, and treating the diazotised product with nitric acid; 50 grams aniline yield 110 grams picric acid.

In the process of Wolfenstein and Bötters (D. R. P. 194883; Eng. Pat. 17521 of 1907; Frdl. 1908-1910, 141, 142) 400 grams benzene, 1350 grams nitric acid (sp.gr. 1.39), and 50 grams mercuric nitrate are mixed and warmed on the water-bath. The products are 380 grams picric acid, 160 grams nitrobenzene, 2 grams *o*-nitrophenol. The nitrobenzene is removed by distillation, leaving crude picric acid as the residue. Oxides of nitrogen may be substituted for nitric acid in presence of either mercury or its salts (D. R. P. 214045).

The Government regulations for the manufacture of picric acid regard it as an explosive except when it contains not less than half its weight of moisture.

**Properties.** Picric acid crystallises from water or alcohol in lustrous, bright-yellow leaflets, and from ether in rhombic prisms melting at 122.5°; it sublimes when cautiously heated, and is very sparingly soluble (Berthelot, Ann. Ch., 1844, 44, 92).

It is sparingly soluble in cold, but more readily soluble in hot, water, 1 part of the acid dissolving in 166 parts of water at 5°, in 86 parts at 15°, 81 parts at 20°, 77 parts at 22.5°, 73 parts at 26°, and in 26 parts at 79° (Marchand, J. pr. Chem. [i.] 44, 92).

The solution is more intensely coloured than the ordinary crystallised salt, and dyes the skin and animal fibres a deep yellow; 1 mg. of acid in a litre of water colours the solution quite appreciably.

Picric acid dissolves readily at ordinary temperatures in alcohol or moist ether, and in about 10 parts of benzene; it is also soluble in concentrated sulphuric acid, forming a colourless solution, the picric acid may be partially precipitated on dilution.

Picric acid can be obtained in colourless crystals on diluting concentrated hydrochloric acid (Ber. 1900, 33, 1128). By washing these crystals with water they develop a yellow colour, and the almost colourless mother liquor also becomes yellower on dilution with water. If ordinary picric acid be dried over concentrated sulphuric acid in a vacuum desiccator, it gradually assumes a lighter colour, and ultimately becomes almost colourless. Pure and perfectly dry picric acid may therefore be considered a colourless compound.

It has been proposed to explain these facts by the dissociation theory; as with other strong acids, ionisation is effected in presence

of a mere trace of water, forming  $C_6H_3(NO_2)_3O-$  and  $H^+$ , the former complex ion being yellow. If, however, to this ionised solid or to its aqueous solution another strong acid like hydrochloric or sulphuric acid is added, then the picric ions associate again, the complex ions disappear as such, and the solution becomes paler. Ordinary or moist picric acid and the fused acid are both yellow; even specimens of the almost colourless acid give an intensely yellow melt. A striking illustration of these facts may be obtained by shaking commercial picric acid with light petroleum; as the solvent is a non-dissociating medium a colourless solution is obtained, but if, however, only little picric acid is present, the petroleum solution be now shaken with water, the solution becomes intensely yellow. Nearly colourless picric acid separates from hot concentrated solutions of light petroleum as white crystals on cooling. Similar bleaching effects on desiccation have been observed on fabrics themselves dyed with picric acid by Dreaper and Stokes (J. Soc. Dyers, Col. 1909, 25, 10).

Anhydrous ethyl ether dissolves picric acid only sparingly, and the solution is colourless until a trace of water be admitted, when the colour develops, and much more picric acid can now be dissolved in the moist ether (Bougault, J. Pharm. Chim. 1903, [iii.] 18, 116).

It has been stated by Vignon (Compt. rend. 1909, 148, 844) that the depth of colour of a picric acid solution varies according to its conductivity. Aqueous solutions dye wool and then become impoverished when their conductivity diminishes to a certain value. This impoverishment can also be brought about by adding hydrochloric acid. The fixation of the dye on the fibre Vignon ascribes to the action of the highly ionised dyestuff, the complex coloured ions combining with the fibre; it would seem, therefore, to be not a salt-forming phenomenon (cf. von Georgievics, Ber. 1906, 39, 1536; Sommerhoff, Zeit. Farb. Ind. 1906, 5, 270).

Stepanoff (Annalen, 1910, 373, 219) states that the solubility of picric acid in water decreases by the addition of hydrochloric acid, until it reaches a minimum when the solution contains roughly 0.5 millimoleculs of picric acid and 150 millimoleculs of the mineral acid in 100 c.c. of solution, after which the solubility increases as the concentration of hydrochloric acid becomes greater. He explains this change as being due to an additive compound of picric acid and hydrochloric acid, which is stable only in definite concentrations of hydrochloric acid, and dissolves readily in this acid when the concentration favourable to the existence of the addition compound is reached (cf. also J. Russ. Phys. Chem. Soc. 1910, 42, 495).

Other solubility measurements in various media, and various other physical properties, have been observed by Findlay (Chem. Soc. Trans. 1902, 81, 1219), Sisley (Bull. Soc. chim. 1902, [iii.] 27, 901), Marchand (J. pr. Chem. 1848, [i.] 44, 91), Dolinsky (Ber. 1905, 38, 1835), Drucker (Zeitsch. physikal. Chem. 1903, 46, 827; 1904, 49, 563), Bougault (J. pharm. Chim. 1903, [vi.] 18, 116), Gorko (Zeitsch. physikal. Chem. 1908, 61, 495).

**Addition-compounds.** Picric acid possesses the property of combining in molecular propor-

tions with many aromatic hydrocarbons and phenols, giving crystalline additive compounds with a fair degree of stability (Fritzsche, J. pr. Chem. [i.] 73, 212; Annalen, 109, 247; Berthelot, Bull. Soc. chim. 1867, 7, 30).

*Benzene* forms such an addition product  $C_6H_6 \cdot C_6H_3(NO_2)_3OH$ , which crystallises in yellow needles, m.p.  $85^\circ$ – $90^\circ$ ; it decomposes at the ordinary temperature in a vacuum desiccator, or by solution in water.

*Naphthalene* forms a molecular compound on fusion with picric acid or on mixing alcoholic solutions of the two components, yielding golden-yellow crystals, m.p.  $149.5^\circ$ ; several eutectic mixtures may also be obtained. It is decomposed by large excess of alcohol (Saposhnikoff and Rdultowsky, J. Russ. Phys. Chem. Soc. 1903, 35, 1073).

The *anthracene* derivative is obtained by mixing concentrated alcoholic solutions of the hydrocarbon and acid, when beautiful ruby-red needles separate having the m.p.  $138^\circ$ ; it is resolved into its components on dissolving in a large volume of alcohol, water, or ether (cf. Behrend, Zeitsch. physikal. Chem. 1894, 15, 183).

*Phenanthrene* yields a stable picric acid derivative, which may be recrystallised from alcohol and obtained in golden yellow crystals, m.p.  $143^\circ$  (Hayduck, Annalen, 1873, 167, 177). Ammonia liberates the hydrocarbon in the pure state, after the removal of separation of phenanthrene.

*Phenol* and picric acid form an additive compound which melts at  $53^\circ$ ; it decomposes at  $100^\circ$  or in a desiccator over sulphuric acid at ordinary temperatures (Goedike, Ber. 1893, 26, 3042). The same author has made a picrate of *acetophenone*, and suggests the rule that substituted phenols, &c., only form picrates when the substituent is at the *ortho*-position.

#### *α-Naphthol picrate*

$C_{10}H_7(OH) \cdot C_6H_3(NO_2)_3OH$  crystallises in orange-yellow needles, m.p.  $189^\circ$ , and is very soluble in alcohol or ether.

The *β-naphthol* derivative exists as yellow needles, m.p.  $155^\circ$ ; readily soluble in alcohol, ether, or chloroform, although decomposed by ammonia. Combination is said to take place according to the law of adsorption, as the amount of compound formed depends on the concentration of the hydrogen ions (Pellet-Jolivet and Henny, Bull. Soc. Chim. 1909, [iv.] 5, 623; cf. also Kuriloff, Zeitsch. physikal. Chem. 1897, 23, 90, 673; 24, 441; and Bruni, Gazz. chim. ital. 1898, 28, ii. 508).

It has been shown by Bruni and Tornani (Chem. Zentr. 1904, ii. 954) that compounds possessing an allyl grouping,  $\cdot CH_2 \cdot CH : CH_2$  in the side chain, like saffrol, methyl eugenol, and apiol, do not combine with picric acid, whilst compounds containing the  $\cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot$  group, such as  $\cdot CH = CH \cdot CH_2 \cdot$  react with it. Olefinic compounds like piperonal, and ketones such as cyclohexanone also form well-defined picrates. Gibson describes the picrate of nitroaniline (Chem. Soc. Trans. 1908, 93, 2100), and Tilden and Forster have prepared a crystalline derivative of *pinene* and picric acid, m.p.  $133^\circ$  (Chem. Soc. Trans. 1893, 63, 1388).

In addition to the above additive products, picric acid forms very characteristic crystalline





1906, ii. 809), who merely mixes potassium iodide and iodate with the picric acid solution, iodine being liberated, which is estimated by titrating with thiosulphate, using starch solution as indicator. For the evaluation of picric acid salts it is necessary to acidify with mineral acid, extract with benzene, evaporate, and redissolve the residue in water before proceeding with the above titration. The use of a potassium iodide solution after bromination with bromine water, in order to determine the amount of halogen absorbed, is recommended by Allen (Chem. Soc. Trans. 1888, 53, 592). Sinnatt has employed Knecht's method of titration with titanous chloride for the estimation of the additive compound with naphthalene (Chem. Soc. Proc. 1905, 18, 297; cf. Colman and Smith, Chem. Soc. Trans. 1900, 77, 128). Picric acid in its compounds with organic bases has been estimated by Kutusow (Zeitsch. physiol. Chem. 16, 505). *g. ptomaines* are readily separated from mixtures by the addition of picric acid and the compound can be weighed; but the author recommends the determination of the combined picric acid colorimetrically either by the spectrophotometer, or, better, by the use of Hoppe-Seyler's double pipette (cf. Zeitsch. physiol. Chem. 16, 505).

A gravimetric determination of picric acid is given by Busch and Blume (Zeitsch. angew. Chem. 1908, 21, 354), depending upon the precipitation of nitron-picric acid, and involving the use of the reagent 'nitron' (described in Ber. 1905, 38, 856). Nitron picric acid, which is very sparingly soluble, consists of lemon-yellow needles, and after drying at 110° is weighed; the weight multiplied by  $\frac{229}{541}$  gives the amount of picric acid present in the solution examined. The method is not applicable in presence of hydrobromic, hydriodic, chloric, perchloric, nitrous, nitric, or chromic acids.

An alternative method of evolution, due to Utz (Zeitsch. anal. Chem. 1908, 47, 140), is recorded, in which picric acid is oxidised with hydrogen peroxide in sodium hydroxide solution, and the nitric acid produced is precipitated as insoluble nitron-nitrate and subsequently weighed: 1 gram = 0.037406 gram of nitrogen.

Picric acid may be quantitatively estimated by precipitation with acridine, since acridine picric acid is very sparingly soluble in cold water (Anschütz, Ber. 17, 439).

**Adulteration.** Commercial picric acid sometimes contains impurities, which either are by-products—e.g. resin, oxalic acid, &c.—formed in its manufacture and subsequently removed by washing, or are fraudulent additions. According to Winckler (Wagner's J., 1858, 461), the following impurities may be recognised thus:—

(1) Resin: dissolve 1 part of picric acid in 60 parts of boiling water, add  $\frac{1}{100}$  of the weight of sulphuric acid and filter. Any resin will be left behind on the filter paper. (2) Oxalic acid: examine the specimen with ammonia, or dissolve 1 part in 100 parts of water, and estimate the amount by precipitating with ammonia and calcium chloride solution. (3) Nitre, or sodium sulphate: treat with alcohol to dissolve the picric acid present, and examine the saline residue by the ordinary method. (4) Sugar:

neutralise with potassium carbonate, evaporate to dryness, and extract the sugar by repeated treatment with alcohol; then examine the alcoholic extract for sugar in the usual way.

Casthelaz (Chem. News, 15, 140) states that common salt and alum are sometimes used as adulterants in addition to the foregoing, and treats the specimen with benzene or ether, which extract the whole of the picric acid, but do not dissolve the oxalic acid and various salts which may be present.

#### USES IN INDUSTRY

**Dyeing.** Picric acid has the property of dyeing animal fibres and tissues directly in an acid bath, but is not fixed by cotton or other vegetable fibres, unless previously mordanted with albumen or with a mixture of aluminium and magnesium acetates; hence it is sometimes used as a means of detecting cotton in undyed silk or woollen fabrics. Its tinctorial powers are great, and it produces on silk and wool a clear, bright yellow, which, compared with most other yellows, appears to have a greenish shade; but, owing to the colour being fast neither to light nor washing, picric acid is now but little used as a yellow dye, although it is frequently employed to produce compound colours with such dyes as benzaldehyde-green, methyl-violet, indigo-carmin, &c.

Picric acid has been used in the preparation of certain other dyestuffs of the nigrosine and induline class; it is fused with various monamines such as aniline and its hydrochloride, in presence of ammonium vanadate, and the spirit-soluble dye converted into water-soluble dye by sulphonation and formation of the sodium salt; a nigrosine colouring matter results. The indulines involve the use of aromatic diamines in a similar manner, and glycerol is added to the melt (D. R. PP. 84293, 84294; Frdl. 1894-1897 440, 451; cf. also Bacovescu, Chem. Zentr. 1908, i. 2034).

Substantive cotton dyes have been prepared from picric and picraminic acids by heating in aqueous solution with sulphur and alkaline sulphides (D. R. P. 116791; Frdl. 1900-1902, 746).

**Tanning.** Its use in the leather industry is mentioned by Watenburger (Leather Manufacture, 1901, 12, 54; J. Soc. Chem. Ind. 1901, 596). After tanning the hides with picric acid solution, they are allowed to drain and then transferred to a 1 p.c. tannin extract for 12 hours; they are afterwards washed, partially dried and fat ligoired, and finished in the usual way. The picric acid is fixed in the grain of the material in a permanently insoluble form.

**Explosives.** Picric acid is usually said to explode on heating, but Berthelot has pointed out (Compt. rend. 105, 1159) that this is only true when very small quantities at a time are suddenly heated, for when heated in any quantity the acid melts and gives off vapours which burn with a luminous flame without explosion; picric acid, moreover, does not under ordinary conditions explode by percussion. The picrates, on the other hand, are readily exploded by heating or percussion, and have been employed as explosives—lead picrate, for example, being used for filling percussion caps (Prat, J. 1874, 1124). Picrates, however, do not



Both yield the dihydrate at 80°, and the anhydrous salt at 150°, the latter being a green powder, which explodes at 335°.

**Potassium salt**  $C_6H_2(NO_2)_3OK$ , is anhydrous. It crystallises from aqueous solutions in yellow iridescent prismatic needles, and explodes at 311°. Sparingly soluble in cold water.

**Silver salt**  $C_6H_2(NO_2)_3OAg$ . Yellow anhydrous salt, exploding feebly at 336°.

**Sodium salt**  $C_6H_2(NO_2)_3ONa$ . Minute, yellow needles, melting at 150°, which is a pale yellow powder, exploding feebly at 310°.

**Strontium salt**  $[C_6H_2(NO_2)_3O]_2Sr \cdot 5H_2O$ , yellow needles, yields *monohydrate* at 80°, and *anhydrous salt* at 200°. Explodes violently at 340°.

**Zinc salt**  $[C_6H_2(NO_2)_3O]_2Zn \cdot 9H_2O$ . Yellow prismatic needles; yields *dihydrate* at 80°, and *anhydrous salt* at 150°, which is a brownish-yellow powder, exploding violently at 350°. The *hexahydrate* has been prepared and also an *octohydrate*.

*Cf.* paper by Kast (Chem. Soc. Abstr. 1911, 100, 852; Zeitsch. ges. Schiess-sprengstoff-wesen, 1911, 6, 7).

A *sodium peroxide derivative* of picric acid  $C_6H_2(NO_2)_3O-ONa$  has been patented as a very powerful explosive (D. R. P. 96855; Frdl. 1897-1900, 47). It is prepared by heating 5 grams of sodium peroxide in 200 c.c. of water containing 15.9 grams of picryl chloride for 2-3 hours. The solution becomes deep brown, and deposits red-brown prisms on cooling, which are sparingly soluble.

A *picra-borate explosive*, described by Billet (J. Soc. Chem. Ind. 1900, 1144), is obtained by heating aqueous solutions of sodium borate and picric acid.

Girard (J. Soc. Chem. Ind. 1900, 1144) gives a new method of preparing picrates for explosives: a mixture of 30 kilos. castor oil and 10 kilos. of powdered picric acid is incorporated with the theoretical quantity of the base in the state of carbonate or oxide: the soluble alkalis are used in solutions of 45°Bé. The oil should be present in not less amount than 5 parts to 10 parts of acid. Metallic oxides may be replaced by oleates, stearates, palmitates, &c., the fatty acids dissolving in the castor oil after reaction. The salts are dissolved out with volatile solvents to avoid the inconvenience attending their recovery from aqueous solution.

#### ETHERS OF PICRIC ACID.

**Methyl pierate**  $C_6H_2(NO_2)_3OCH_3$  (*trinitro-anisole*). Yellow monoclinic tables, m.p. 64° (Post and Mehrtens, Ber. 8, 1552; Frdl. 1879, 514). Obtained by nitrating anisole. Decomposed by strong potassium hydroxide giving picric acid, and with ammonia giving trinitraniline (Salkowski, Annalen, 1874, 174, 259).

**Ethyl pierate**  $C_6H_2(NO_2)_3OC_2H_5$ . Colourless needles, m.p. 78.5°. Müller, Annalen, 1867, 141, 80; Willgerodt, Ber. 1879, 12, 1277). Obtained from methyl ether on recrystallising from ethyl alcohol (Boos, Amer. Chem. J. 20, 449).

**Phenyl pierate**  $C_6H_2(NO_2)_3OC_6H_5$ . Needles, m.p. 153°. Prepared from picryl chloride and

potassium phenate in aqueous alcoholic solution (Willgerodt, Ber. 1879, 12, 1278).

**Acetyl pierate**  $C_6H_2(NO_2)_3O-OC-CH_3$ . Deep yellow crystals, m.p. 77°. Decomposed giving acetic acid, at 120°. Combines with picric acid and acetic anhydride (Tommasi and David, Annalen, 169, 167; Heinke, Ber. 1898, 31, 1400; v. Pechmann, Ber. 1900, 33, 629). Very soluble in warm alcohol or ether.

#### OTHER DERIVATIVES.

**Picryl chloride**  $C_6H_2(NO_2)_3Cl$ . Crystallises from ether in amber-yellow tables; from alcohol in almost colourless plates, m.p. 83°. Obtained by the action of phosphorus pentachloride on picric acid. Like picric acid itself, it combines with aromatic hydrocarbons, forming additive products (Pisani, Annalen, 1854, 92, 326; Liebermann and Palm, Ber. 1875, 8, 378).

**Picryl bromide**  $C_6H_2(NO_2)_3Br$ . Elongated, pale-yellow plates, m.p. 122°-123° (Jackson and Earle, Amer. Chem. J. 1903, 29, 212). Obtained by nitrating bromobenzene.

**Picramide**  $C_6H_2(NO_2)_3NH_2$  (trinitraniline). Prepared by action of ammonia on picryl chloride or on ethyl pierate. Dark yellow, monoclinic tables, m.p. 188° (Hepp, Annalen, 1882, 215, 350; Salkowsky, Annalen, 1873, 165, 187).

**Picramic acid**  $C_6H_2(NO_2)_2(NH_2)OH$ . Obtained by reduction of picric acid with ammonium sulphide or other mild reagents. Red crystals, m.p. 169° (Girard, Annalen, 1853, 88, 281; Pugh, *ibid.* 1855, 96, 83; Stuckenberg and Rudolf, J. pr. Chem. [ii.] 48, 425). Used formerly as a brown dye.

*iso*Purpuric acid (picrocyaminic acid, or *grenat brown*) *v.* *iso*-PURPURIC ACID.

**PICRIN** *v.* DIGITALIS.

**PICROGLYCION** *v.* DULCAMARA.

**PICROPODOPHYLLIC ACID** and **PICROPODOPHYLLIN** *v.* *Podophyllum resin*, art. RESINS.

**PICROTIN, PICROTOXIDE** *v.* PICROTOXIN.

**PICROTOXIN**. A poisonous crystalline compound, somewhat allied in its physiological action to strychnine, which occurs in 'Cocculus Indicus,' the small, berry-like fruit of *Anamirta paniculata* (Colebrooke) (Bentl. a. Trim. 14), a climbing shrub of Eastern India and the Malayan islands. The drug does not find much favour in Western medicine, but is employed in India. Here it is better known for its power of stupefying fish and causing them to rise to the surface of the water in a state of intoxication, and as a reputed adulterant of malt liquors. On account of its poisonous properties, it sometimes becomes necessary to search for it in beer.

The small, black, ovoid fruit consists of a rough, tasteless pericarp, enclosing a reniform seed, which has an oily and bitter taste. The pericarp does not contain picrotoxin, but Pelletier and Couerbe isolated from it two crystalline compounds: *menispermine*, a base, which melts at 120° and forms a crystalline sulphate, and *paramenispermine*, a neutral constituent which melts at 250°, together with a brown mass, *hypopicrotoxic acid*, which softens at 106° (Ann. Chim. Phys. [ii.] 54, 196). Half the weight of the seed is stearin. The *picrotoxin* exists to the extent of 0.4 to 1.0 p.c. It was discovered in 1812 by Boullay (J. Pharm. Chim. [i.] 4, 5).

To prepare picrotoxin, the method of Barth (J. pr. Chem. [i.] 91, 155; J. 1863, 586) and Barth and Kretschy (Monatsh. 1, 98) is usually followed. The seed is exhausted with boiling alcohol, the solution evaporated, and the fatty residue extracted with water. The residue is then treated with lead acetate, the filtrate, after removal of excess of lead by means of sulphuretted hydrogen, is concentrated, when crystals of impure picrotoxin separate. These are purified by successive crystallisations from benzene and from water. Sometimes the seed is extracted with light petroleum in the place of alcohol (Marek, Arch. Pharm. [iii.] 26, 269).

According to Barth and Kretschy (Sitz. Ber. 81, 7; Ber. 13, 1243), crude picrotoxin is a mixture of three compounds—picrotoxin, picrotin, and anamirtin—which are separated by fractional crystallisation from water and from benzene. This is, however, disputed by Paternò and Ogliastro-Todaro (Gazz. chim. ital. 10, 36; 11, 49; Ber. 14, 539), who regard the compounds named as decomposition products of a perfectly definite picrotoxin. Retaining the term picrotoxin for the original substance, these chemists propose picrotoxinin as a name for the mixture of Barth and Kretschy. The composition of picrotoxin is thus explained:  $C_{30}H_{34}O_{13}$  (picrotoxin) =  $C_{15}H_{18}O_6$  (picrotin of B. and K., previously called hydrate of picrotoxin by P. and O.) +  $C_{15}H_{16}O_7$  (picrotoxinin of Paternò and Ogliastro-Todaro).

The investigations of Paternò and Ogliastro-Todaro are supported by the investigations of Schmidt and Löwenhardt (Ber. 14, 817) and Schmidt (Annalen, 222, 313), whilst Barth and Kretschy have replied maintaining their original view (Monatsh. 5, 65). Meyer and Bruger (Ber. 31, 2958) also have come to the conclusion that the picrotoxin of Paternò and Ogliastro-Todaro of Schmidt is not a definite compound.

Investigators find that the recrystallised commercial compound is merely a mixture of picrotoxinin and picrotin in definite, but not molecular proportions, namely 54–55 p.c. of picrotoxinin and 45–46 of picrotin. It may be partially separated into the two constituents by boiling with benzene or chloroform or by treatment with concentrated sulphuric acid (cf. Angelico, Gazz. chim. ital. 31, 645) or with bromine water.

Recrystallised commercial picrotoxin, the picrotoxin of Paternò and Ogliastro-Todaro and of Schmidt, consists of brilliant rhombic prisms, which melt at 199°–200° (Sch.). It is intensely bitter and poisonous. It is very soluble in hot water, alcohol, or benzene, and sparingly so in ether or chloroform.

By the addition of bromine water to a hot aqueous solution of picrotoxin, monobromopicrotoxinin separates, and on evaporating the filtrate, picrotin is obtained, and can be purified by repeated extraction with small quantities of hot chloroform and recrystallisation from water (M. and B.). Picrotin  $C_{15}H_{18}O_6$  forms small felted needles or thick rhombic prisms, m.p. 248°–250°, which are readily soluble in absolute alcohol or acetic acid, but only sparingly in ether, chloroform or benzene. It reduces Fehling's solution and ammonio-nitrate of silver. It possesses a bitter taste, but is not poisonous. Benzoylpicrotin  $C_{15}H_{18}O_6 \cdot C_7H_5O_2$  forms colourless needles, m.p. 236°; a dibenzoyl derivative, m.p. 247°–248°, is obtained by the action of benzoyl

chloride at 190°. Acetylpicrotin  $C_{15}H_{17}O_6 \cdot Ac$ , m.p. 244°–245°, is obtained by treatment with the compound and acetic anhydride, and Ogliastro-Todaro as diacetylpicrotoxinin. When warmed with fuming nitric acid, picrotin yields a nitro derivative anhydronitropicrotin  $C_{15}H_{15}O_6NO_2$ , m.p. 260° (M. and B.). On oxidation, two isomeric acids  $C_{15}H_{14}O_8$  are obtained  $\alpha$ -picrotinic acid, m.p. 245°, and  $\beta$ -picrotinic acid, m.p. 254° (Angelico, Gazz. chim. ital. 39, i. 296; 40, i. 391; 41, ii. 337; Atti, R. Accad. Lincei, [v.] 19, i. 473). Phosphorus pentachloride acts as a dehydrating agent on picrotin converting it into anhydropicrotin  $C_{15}H_{16}O_6$ , m.p. 317° (decomp.), which differs from picrotin by not reducing Fehling's solution (Hörmann, Ber. 43, 1903). Picrotoxinin  $C_{15}H_{16}O_7 \cdot H_2O$ , the 'picrotoxin' of Barth and Kretschy, is best obtained by the reduction of bromopicrotoxinin with zinc and acetic acid. Picrotoxinin crystallises in rhombic tables, which become anhydrous at 100° and melt at 200°–201°. It is bitter and exceedingly poisonous. It dissolves readily in hot water, benzene, alcohol, ether, or chloroform; it is also soluble in alkalis, but is not precipitated on the addition of acids. It develops an intense orange-red colouration, and when hydrogen chloride is led into an ethereal solution of the compound polymerisation occurs and picrotoxinide, m.p. 308°–310°, is formed. Bromopicrotoxin  $C_{15}H_{15}BrO_6$  is most readily obtained by adding bromine water to a hot nearly saturated aqueous solution of picrotoxinin until the solution remains permanently yellow. It separates from

ether as a crystalline benzoyl derivative, which melts at 237°–238° (Sch.). On reduction by hydriodic acid and phosphorus both picrotin and picrotoxinin yield picrotoxic acid  $C_{15}H_{14}O_8$ , m.p. 134°, and also a ketone  $C_{14}H_{16}O_3$  (cf. Paternò and Ogliastro-Todaro, Gazz. chim. ital. 31, 645). Anamirtin  $C_{15}H_{16}O_7$  occurs in the seed, and collects in the mother liquors in the preparation of picrotoxin, distinguished by its sparing solubility in chloroform and benzene. It is not bitter, is not poisonous, and does not reduce Fehling's solution or ammonio-nitrate of silver. When heated, it chars without melting at 280° (Barth and Kretschy).

Cocculin  $C_{15}H_{20}O_{10}$  is another constituent of the seed, discovered by Löwenhardt (Annalen, 222, 353), and occurs only in small proportions. It is found in the alcoholic mother liquors in the preparation of picrotoxin. It crystallises in needles, is difficultly soluble in hot, and insoluble in cold, water, alcohol, or ether, and does not give the colour reactions of picrotoxin.

For the detection of picrotoxin in beer the chemical reactions are not of much use. Extracts are prepared which are tested physiologically (cf. Langley, Amer. J. Sci. [ii.] 34, 109; Schmidt, J. 1862, 629; Köhler, J. 1868, 796, 893; Blas, J. 1872, 936; Depaire, J. 1872, 946; Palm, Zeitsch. anal. Chem. 24, 556). A. S.

#### PICROTOXININ v. PICTOTOXIN.

PICRYL BROWN. A colouring matter belonging to the class of yellow, orange-yellow, and brown dyes introduced by Nölting and v. Salis-Mayenfeld, and obtained either by sulphonating

nitro derivatives of secondary and tertiary aromatic amines, or by the action of such compounds as dinitrochlorobenzene, trinitrochlorobenzene (picryl chloride), chlorotetratranaphthalene, &c., on the sulphonic acids of aromatic amines (D. R. P. 22268 of Aug. 31, 1882, expired Jan. 1887; W. J. 1883, 545). It is prepared (1) by sulphurating trinitrophenylamine (cf. *Monatsh.*, Ber. 7, 1249) with  $2\frac{1}{2}$  times its weight of 40 p.c. anhydrosulphuric acid, or with 5 times its weight of sulphuric acid of 66°Bé., or (2) by boiling a concentrated aqueous solution of 3 parts sulphanic acid, 3 parts picryl chloride, and  $2\frac{1}{2}$  parts of sodium acetate. Picryl brown is soluble in water, and in an acid bath dyes silk and wool yellow.

# PIGMENTS (*L. pigmentum*, from *pingere*).

**Definition.** Insoluble coloured powders, yielding paints when admixed with suitable media. This definition excludes dyes or stains, which are soluble in the vehicles used.

**History.** The use of pigments can be traced back to the earliest times, even to palæolithic times. The Chinese, before the Christian era, the Egyptians, excelled in pictorial art. In Assyria, in Lydia, from the eighth century B.C., and by the Ionians and Phœceans, from about the sixth century B.C., painting was skilfully practised and held in high esteem. Cimon of Cleonæ, his successors Polygnotus of Thasos (463 B.C.), Apelles of Colophon, and Zeuxis of Heraclea, and other early painters worked chiefly in fresco and tempera, with a limited range of pigments, nearly all mineral. Encaustic was not commonly practised until after the time of Alexander the Great. The pigments were mostly the ochres, red lead, cinnabar, orpiment, chalk, gypsum, lapis lazuli (?), indigo, carbon, and certain special colours, such as 'Egyptian blue' (a copper fritt or glass) and 'Tyrian purple.' From the accounts given by Pliny the Elder and Theophrastus, it would appear that a blue prepared from lapis lazuli was not known in classical times. Red lead, or minium, was used for the coloured statue of Jupiter, set up by King Tarquinius Priscus in the Roman Capitol. The vegetable colours anciently used have probably for the most part decayed, leaving no traces; but a pink madder lake and a yellow lake have been discovered among the pigments of the ancient Egyptians. Until quite recent times, artists prepared and ground their own pigments; this work is now almost invariably done by the colour manufacturer.

**Properties.** Pigments must be durable; insoluble; inert, i.e. unaffected by one another; in general indifferent to the media; of good body and covering power; easy to manipulate with vehicles on the palette, and of a fine shade of colour. Certain pigments, when used in oil paints, possess the additional property of facilitating the drying of the oil with which they are mixed: white lead is a conspicuous example. The characteristics here laid down are those usually desired: but there are exceptions in the case of pigments used in art. Thus some of the colours most valued by artists possess considerable transparency; in water-colour work the conditions of drying are altogether different from those in oil-painting.

In regard to durability or permanence, an

ideal pigment should be fast to light, unchanged by exposure to the atmosphere and moisture, proof against the action of acids or alkalis, and unaffected by sulphur compounds, such as sulphuretted hydrogen or carbon disulphide. Of the large number of pigments known, comparatively few fulfil all these requirements. In particular circumstances, especial qualities become necessary: thus, for decorative and fresco work, pigments must be fast to lime, for ceramic use they must be proof against fire, and if the paintings have to be lacquered, they must be fast to varnish.

By some authorities, the term 'permanence' is restricted to unalterability of hue, and 'durability' to the conservative effect of a pigment upon the surface which it covers. Pigments unchanged by admixture with other colours are said to possess inertia. Covering power and body are not convertible terms. Spreading or covering power applies to the capability of being extended or spread over a large surface. Body refers to opacity.

After an account has been given of the origin, composition, and salient characteristics of the pigments in general use, the subject of stability or permanence will be dealt with more fully, and the colours will be divided into groups, according to the degrees of permanence.

## Origin, classification,

The majority of pigments, whether artificially prepared, or obtained almost directly from natural sources, such as the ochres and other coloured earths, are of mineral or vegetable origin. A few, such as sepia, purpur, mummy (sometimes), and the preparations derived from the several species of *Coccus*, are animal products.

The native earths are levigated, dried, sifted, graded, ground and, in certain cases, calcined. Most artificially prepared pigments are manufactured by wet precipitation methods: instances are chrome yellow, Prussian blue, and antimony vermilion. In a large number of cases, however, dry processes and various temperatures are required; e.g. artificial ultramarine, vermilion, and ivory black. Lakes are made by precipitating organic colouring matters, which may be of vegetable or animal origin, and at the present time are frequently so-called coal-tar colours, in conjunction with alumina, lime, and the like. Special methods are employed in the manufacture of certain pigments, such as white lead.

The classification of the mineral pigments, adopted in this article, strictly follows the ordinary grouping of the metals present, as they are separated in analysis. Siliceous and carbonaceous pigments follow, and organic colouring matters are described last. When possible the colours follow in the order: white, yellow, red, green, blue, brown, and black.

**Pigments containing mercury.** Three mercury pigments only will be included in the following summary.

**Vermilion, cinnabar, zinnober,** mercuric sulphide,  $HgS$ : a brilliant colour, usually prepared from its elements, which are at first caused by simple attrition or other means, to combine into a black mass, called 'ethiops,' chiefly amorphous mercury sulphide, together with free sulphur. The molecular change into the scarlet sulphide

is effected by sublimation, treatment with alkalis, alkaline polysulphides, or the like.

Numerous other methods of manufacture have been suggested and practised. Vermilion possesses great opacity, but dries imperfectly in oil and is liable to separate from the vehicle used. It is permanent in oil, durable in tempera and fresco, but changeable in water colour by the influence of the solar rays. Sulphuretted hydrogen does not affect it, and in oil it can be mixed with all except certain copper pigments. As it is a volatile compound, it is ineligible for enamels and ceramic ware.

*Brilliant scarlet, Royal scarlet, Pure scarlet,* mercuric iodide,  $\text{HgI}_2$ : extremely brilliant as a pigment and of good body, but fugitive in oil, useless in water colour, immiscible with many other pigments, and too costly for practical purposes.

*Mercurous chromate*  $\text{Hg}_2\text{CrO}_4$ , and *mercuric chromate*  $\text{HgCrO}_4$ , red, highly alterable products, obtained in the wet way by double decomposition. Nearly valueless as pigments, although fine and attractive colours.

**Pigments containing lead.** Of high importance among the lead pigments and, indeed, among commercial pigments generally, is *white lead*, called also *Kreins* or *Kremnitz white*, *Berlin white*, *Silver white*, *Cerussa alba*, *Céruse*, *Bleiweiss*, *Blanc de Plomb*, *Blanc d'argent*, and *Flake white*,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . This basic carbonate of lead is one of the most rapidly drying pigments commonly used in oil; it possesses great opacity and covering power, and is facile in working. Miscible with most durable colours, it promotes the drying of many which have slight siccativ qualities of their own. Unfortunately, white lead is highly poisonous, its manufacture is attended with risk to the operatives, it is readily discoloured by sulphuretted hydrogen, and used with oil it emits a nauseous odour. Numberless substitutes have been proposed, of which perhaps lithopone, zinc oxide, and 'non-poisonous white lead,' are the best known. The supersession of lead products by zinc whites is undoubtedly extending apace.

'Non-poisonous white lead,' or *patent white lead*, and 'sublimed white lead' are composed chiefly of lead sulphate, with small proportions of lead and zinc oxides. The last-named is a basic sulphate with some zinc oxide. These products are little affected by sulphuretted hydrogen, and are virtually non-poisonous: but the covering power of a lead sulphate pigment is less than that of white lead, and the drying quality is inferior.

*Lead oxychloride*  $\text{PbCl}_2 \cdot \text{PbH}_2\text{O}_2$ , sometimes called *Pattinson's white lead*, is occasionally used as a white pigment, as also have carbonate, sulphite, hydroxide, and other salts of lead. All are less satisfactory than the basic carbonate.

*Turner's yellow, Cassel yellow, Montpellier yellow*, or *Verona yellow*,  $\text{PbCl}_2 \cdot 7\text{PbO}$ , is another basic lead chloride, now superseded by chrome yellows.

... respectively, yellow and ... monoxide,  $\text{PbO}$ . The monoxide is now scarcely used as a pigment, but as a drier is of considerable importance. Large quantities are used by potters, glassmakers, and rubber manufacturers.

*Red lead, Orange lead, minium, mennige, Paris red*,  $\text{Pb}_3\text{O}_4$ , sometimes  $\text{Pb}_4\text{O}_6$ , a fine orange-red pigment, which very quickly dries in oil but is discoloured by sulphuretted hydrogen, and is incompatible in admixture with certain sulphur-containing pigments, such as lithopone and cadmium yellow. As a priming coat, in conjunction with white lead for ordinary work, it is extremely useful. *Orange mineral* is a less dense form of red lead.

*Sublimed blue lead* is a mixture of basic sulphate,  $2\text{PbSO}_4 \cdot \text{PbO}$ , with lead suboxide, sulphide, oxide, and carbon. It is used to a considerable extent as a protective pigment.

**Pigments containing silver.** The metal in a finely divided state has occasionally found employment as a pigment, and the use of the chromate,  $\text{Ag}_2\text{CrO}_4$ , has been proposed. Costliness and extreme sensitiveness to sulphuretted hydrogen, are sufficient deterrents to a common application of silver pigments.

**Pigments containing copper.** *Vandyke red*, copper pyrophosphate,  $\text{Cu}_2\text{P}_2\text{O}_7$ , is a brownish-red pigment, occasionally used in artistic painting, but it is untrustworthy and liable to darken.

*Vert de Gris, Verdigris, Vert de Montpelier, Grünspan*, basic copper acetate, varies in hue according to the basicity of the compound. Green verdigris, of the brightest tint, is  $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$ ; blue verdigris is  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$ : but other basic acetates are known and the commercial pigment is a variable mixture of several of these salts. It is made by the action of acetic acid upon copper in the presence of air and moisture. This pigment is useless in water-colour painting, injured by sulphuretted hydrogen, carbon dioxide, and moisture, immiscible with sulphide and some other pigments, and is a powerful poison. In oil it dries well, but is only permanent if 'locked up' by the presence of a large quantity of a resinous varnish.

*Mountain green, Green verdier, Malachite, Mineral green, or Berggrün*, the natural green hydroxycarbonate of copper,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . This is the mineral malachite, finely ground, and is known to have been used by the Græco-Roman artists. As an oil-paint it is moderately durable, but it is liable to darken and assume a brownish or olive tint, and for water-colour it is unsuitable. It will blacken if mixed with cadmium yellow, ultramarine, &c., and is highly sensitive to sulphuretted hydrogen.

*Schweinfurt green, Mitis green, Vert Paul Véronèse, Vert de Paris, Emerald green*, cupric aceto-arsenite,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3(\text{CuAs}_2\text{O}_7)$ , is an exceedingly fine but very poisonous colour, prepared by heating together verdigris, water, and arsenious oxide, the precipitate formed being washed and dried. Inadvisable for use as a water-colour, it is durable in oils, but must not be mixed with sulphide pigments, such as cadmium yellow and ultramarine, nor exposed to sulphuretted hydrogen, which quickly darkens it. Emerald green is somewhat deficient in body and dries slowly. It is not trustworthy for tempera or fresco work.

*Scheele's green*, a basic copper arsenite, varying somewhat in composition, is a pale green pigment of an extremely poisonous character, and is now seldom used. Sulphuretted hydrogen and sulphide pigments are

even more injurious to it than to Schweinfurt green.

*Brunswick green* was formerly basic chloride of copper,  $\text{CuCl}_2 \cdot 3(\text{CuO}, 4\text{H}_2\text{O})$ , now not used as a pigment. The name is now applied to a mixture of Prussian blue, chrome yellow and barytes.

*Mountain blue*, *Blue verditer*, *Chessylite*, *Azurite*, *Blue ashes*, or *Bergblau*, the natural blue hydroxycarbonate of copper,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . Both this and the green (above described) have been manufactured, but not with conspicuous success. Blue verditer is not permanent, and is a pigment little used, artificial ultramarine and cobalt having superseded it.

*Lime blue* and *Bremen blue* are essentially copper hydroxide,  $\text{Cu}(\text{OH})_2$ , associated with calcium sulphate and copper carbonate respectively: both were formerly much used in decorative work. Blue lakes from coal-tar dyes and artificial ultramarine have virtually driven these pigments off the market.

Stannate, phosphate, borate, silicate, and other salts of copper have been tried as pigments, but not very successfully.

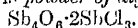
**Pigments containing cadmium.** *Cadmium yellow*, *pale cadmium*, *orange cadmium*, *Orient yellow*, *radiant yellow*, *aurora yellow*, &c., are cadmium sulphide,  $\text{CdS}$ . The cadmium pigments, if free from uncombined sulphur, may safely be mixed with white lead in oil; and, being themselves unaffected by it, they hinder the darkening that gas. Light, air, and moisture have little effect upon the pure cadmium colours when used in oil-painting, but the paler shades are extremely fugitive in water-colour, and the presence of free sulphur is very detrimental since it enhances the tendency to fade. Cadmium pigments are entirely incompatible with the copper greens and blues, and exert a darkening action upon Naples yellow, chrome yellow, Cassel or Turner's yellow, and the like.

*Neutral orange*, *Penley's neutral orange*, is a mixture of cadmium sulphide with Venetian red.

**Pigments containing bismuth.** *Pearl white*, basic bismuth nitrate,  $\text{Bi}(\text{OH})_3\text{NO}_3$ , or  $[\text{Bi}(\text{NO}_3)_3 \cdot 2\text{Bi}(\text{OH})_3]$ , is of little value as a pigment, owing to its susceptibility to the action of sulphuretted hydrogen, which darkens it more rapidly than lead-compounds. Bismuth white was formerly used as a face-powder with somewhat doubtful advantage.

Another bismuth salt,  $6\text{BiOCl} \cdot \text{As}_2\text{O}_3$ , or  $[2(\text{BiCl}_3 \cdot \text{Bi}_2\text{O}_3) \cdot \text{H}_2\text{O}]$ , is called *pearl white*, a name which has also been applied to indigo-tinted flake white.

**Pigments containing antimony.** *Antimony white*, antimonious oxide,  $\text{Sb}_2\text{O}_3$ , finds employment as a substitute for flake white, particularly on the Continent. In oils, especially, this pigment is durable and trustworthy. Another antimony white is *powder of algaroth*



*Antimony yellow*, true *Naples yellow*, *Jaune d'Antimoine*, *Giallo di Napoli*, is basic lead antimoniate,  $\text{PbO} \cdot \text{Sb}_2\text{O}_3$ , and is now usually prepared by heating together potassium antimonyl tartrate, lead nitrate and sodium chloride. The product is cooled, washed, and ground. Numerous other processes have been used.

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Naples yellow is fast to light, but is readily attacked by sulphuretted hydrogen, even in oil-painting; is discoloured by contact with iron and is inadmissible in conjunction with indigo and various other organic pigments, such as the yellow lakes and cochineal products. Naples yellow, or an allied antimonial yellow, has been used for many centuries in enamels and pottery ware. It is unsuitable for water-colour painting. Several imitations of this pigment are, or have been, in the market: one is a mixture of cadmium yellow with zinc white; another was a variety of yellow ochre (Church).

*Antimony vermilion*, *antimonzinnober*, antimonious sulphide,  $\text{Sb}_2\text{S}_3$ , or oxysulphide,  $2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$ , is a fine red pigment of satisfactory covering power, but limited application owing to its sensitiveness to dilute alkalis and acids. The methods of manufacture are based upon the interaction of the alkaline or alkaline earth antimonates and antimonious chloride. An orange variety of this pigment, *antimony orange*, is made by using sulphuretted hydrogen as the precipitant.

**Pigments containing arsenic.** Those in which arsenic is associated with copper have already been considered. There remain the arsenic sulphides:—

*King's yellow*, *Royal yellow*, *arsenic yellow*, *arsenic pigment*, arsenic trisulphide,  $\text{As}_2\text{S}_3$ , but fugitive and extremely poisonous pigment, immiscible with lead, mercury, and copper compounds, and now almost entirely superseded by the corresponding arsenates. It is prepared by the precipitation of arsenic acid.

*Arsenic red*, *arsenic orange*, *realgar*, arsenic disulphide,  $\text{As}_2\text{S}_2$ . This pigment, prepared by a fusion and sublimation-method, is also highly poisonous and generally unsuitable for artists' use.

**Pigments containing tin.** *Tin white*, stannic hydroxide or orthostannic acid,  $\text{Sn}(\text{OH})_4$ , is used in enamel- and glass-making, but scarcely at all for ordinary decorative or artistic work. To a very considerable extent it has taken the place of bismuth subnitrate and oxycarbonate as a face-pigment.

*Mosaic gold*, *aurum musivum* or *mosaicum*, 'Bronze powder,' stannic sulphide,  $\text{SnS}_2$ , a lustrous yellow scale-preparation, made by heating a mercury-tin amalgam together with sulphur and ammonium chloride; or a mixture of tin monosulphide,  $\text{SnS}$ , with mercuric chloride is heated. Another 'bronze' is prepared by fusing together stannic oxide and sulphur. A fused mixture of tin and bismuth, to which mercury is added before the liquid has cooled, yields a silver-tinted metallic pigment.

Other compounds of tin, such as 'tin salt' (stannous chloride,  $\text{SnCl}_2$ ), stannic chloride,  $\text{SnCl}_4$ , 'pink salt,'  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$ , and sodium stannate,  $\text{Na}_2\text{SnO}_3$ , are not used as pigments, but are of the lake-colours.

**Pigments containing gold.** The use of finely divided metallic gold, whether in the form of leaf, or otherwise, by mediæval artists, monkish scribes, and others, in pictures and illuminated manuscripts, also in the colouring of crimson glass, is well known.

*Cassius' purple*, gold stannate,  $\text{Au}_2\text{SnO}_3 \cdot \text{SnSnO}_3 \cdot 4\text{H}_2\text{O}$  or  $\text{Au}_2 \cdot 3\text{SnO}_2$ , is used in glass-ware and ceramic art.

T



**Pigments containing aluminium.** The metal, finely powdered, now receives a wide application as the pigmentary constituent of aluminium paint.

*Kaolin, China clay*, hydrated aluminium silicate,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , is of an unalterable white, and is what deficient in covering power, but in water-colour and tempera painting it is a very serviceable white pigment, and may fulfil the function of a 'filler.' Thus, a 'Chinese white,' for water-colour painting, may contain 3 parts of kaolin to 1 part of zinc oxide. The process of manufacture consists in levigating and drying the natural clay, the main impurities in which are flakes of undecomposed mica and crystals of quartz. Kaolin is much used in the manufacture of paper, and it is an inexpensive carrier for lake-pigments.

*Alumina*  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , though not used as a pigment alone, is a component of many lakes, and occasionally forms part of various composite white pigments, such as satin white, *blanc fixe*, and the like.

*Ultramarine, Bleu d'Outremer*, one of the most permanent, trustworthy, and beautiful of pigments, was formerly obtained exclusively from the rare and costly mineral *lapis lazuli*, a variety of *haüyne*, by an elaborate and tedious elutriation method. The chief constituents of ultramarine are alumina, soda, silica, and sulphur. The formula is doubtful, but may be  $\text{Na}_{10}(\text{Al}_3\text{Si}_5\text{O}_{22})\text{S}_2$  (Brögger and Backlund). It was first met succeeded in manufacturing artificial ultramarine, a pigment little inferior to the natural product of the same composition, equally permanent both in oil and water-colour painting, and moderate in price. Several varieties of artificial ultramarine are made: sulphate ultramarine, which possesses a pale greenish-blue shade; soda ultramarine, poor in silica, the purplish-blue product most in use; and soda ultramarine, rich in silica, a pigment mostly used by paper-makers. *Lime green* or *green ultramarine* is the first stage in the manufacture, and is the colouring ingredient of green water-paints. By roasting with sulphur, green ultramarine is 'coloured,' i.e. it is caused to assume the azure tint. Other varieties of ultramarine than those mentioned are *red*, *violet*, and *black*. The raw materials used in the manufacture of ultramarine are kaolin, silica, soda, carbon, sulphur, and sodium sulphate. *Mineral grey* and *ultramarine ash* are grey and bluish-grey residual products from the processes of treatment of the mineral *lapis lazuli*.

*Ultramarine violet* is obtained when the soda blue is heated with sal ammoniac for many hours at a temperature of about  $150^\circ$ . Further heating with steam and hydrochloric acid converts the violet pigment into *ultramarine red*.

**Pigments containing iron.** *Yellow ochre*, *mineral yellow*, *Roman ochre*, *Oxford ochre*, *stone yellow*, *brown ochre*, *golden ochre*, *Chinese yellow*, &c., are silicious and argillaceous earths, often containing as impurities lime, barium, and other metallic salts, but all owing their yellow or brown colour to the presence of hydrated ferric oxide. These colours, which are prepared for the market by careful sampling and elutriation, are mined in many parts of the world, are

exceedingly lasting, have no effect upon other pigments, are not injured by light or by impure atmospheres, and they can be used with any medium. Ochres vary in opacity, as they vary in composition: most of them possess fair covering power. Pigments of this class were used by the ancient Egyptians, Assyrians, Greeks, and Romans.

*Raw Sienna, Terra di Siena, Italian earth*, is a browner-tinted, manganiferous yellow ochre, occurring in Tuscany, in the vicinity of Rome, Cyprus, and elsewhere. Some American siennas are of very serviceable quality. Raw sienna is fitted for oil, water-colour, tempera, and fresco-painting.

*Burnt Sienna* is a pigment of an orange-brown tint, and suitable for every sort of painting. It is made by cautiously calcining raw sienna.

*Red ochre, Scarlet ochre, Red chalk, Ruddle, Bole, sinopis, Terra rosa*, &c., are varieties of the native anhydrous ferric oxide, or red hæmatite,  $\text{Fe}_2\text{O}_3$ . All are durable pigments and good driers.

*Indian (or Persian) red* is, in strictness, a native product (also hæmatite), of a somewhat purplish shade, imported from the East. But some so-called *Indian red* is manufactured by calcining ferrous sulphate (copperas, or green vitriol),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , or by roasting yellow ochre for about 12 hours.

*Light red, Burnt ochre, Brun rouge*, also, is calcined yellow ochre. The period of heating is 10 hours. This pigment is an opaque, permanent, and innocuous colour, of a scarlet tint, tempered by shades of brown and grey.

*Venetian red, Colcothar, Caput mortuum vitrioli, Crocus, Rouge*. The natural pigment known as Venetian red is a variety of red hæmatite, of a purer red than either *light red* or *Indian red*, but the artificial products are obtained by calcining copperas, or the ochres. Time, in the case of the ochres, about 8 hours; temperature, a low red heat. If pure, Venetian red is uninjurious to other permanent colours, but soluble salts, especially sulphates and traces of acid, must be absent. The last-named exert a detrimental action upon organic pigments, such as indigo; upon the vehicle used; and also on the surface coated, if this chance to be of metal.

*Prussian brown*, a rarely used pigment consisting of ferric oxide in admixture with carbon and made by carefully calcining Prussian blue. It is permanent and a good drier.

*Mars yellow, Mars orange, Mars red, Mars brown, and Mars violet*. These are artificial ferruginous pigments, prepared by precipitating salts of iron, with or without the addition of alum, by milk of lime or an alkaline hydroxide, drying, and calcining the precipitates at various temperatures, according to the colour required. The Mars pigments present no particular advantages over the ordinary iron yellows and reds, and they may be somewhat injurious to certain of the madder pigments.

*Terre verte, Verona green, Veronese earth, Green earth*, &c., are pale, bluish-green, natural pigments, consisting essentially of an alkaline and magnesian ferrous silicate; but as the localities are numerous, considerable variations in composition are observed. *Terre verte* is one

of the most inert and permanent pigments used by artists, but it is deficient in body and intensity of hue. It is available for painting in oil, water-colour, tempera and fresco.

*Prussian blue, Chinese blue, Antwerp blue, Berlin blue, Paris blue, soluble blue, bronze blue, Saxon blue, &c.* This pigment occurs in several forms. Commonly, it is a mixture of potassium ferric ferrocyanide,  $K_3Fe_3Cy_{12}$ , with ferric ferrocyanide,  $Fe_3Cy_{18}$ ; but the most permanent form is ferric ferrocyanide,  $Fe_3Cy_{18}$ . Some of the varieties named, such as Antwerp blue and Paris blue, contain other ingredients and are inferior to the true Prussian blue, which is an intense colour with a slight greenish shade, is permanent, miscible with other pigments and useful both in oils and water-colour. It is not available for fresco-work or enamels. Though liable to fade in a strong light, it recovers its intensity of hue when kept in the dark for a while.

**Pigments containing chromium.** *Chrome yellow*, normal lead chromate,  $PbCrO_4$ , is a salt of a full yellow hue, prepared by a simple precipitation process. Usually, mixed or diluted chrome yellows are met with in commerce, lead sulphate, barium sulphate, or gypsum, being associated with the lead chromate: examples are  $PbCrO_4 \cdot PbSO_4$  and  $PbCrO_4 \cdot 2PbSO_4$ . *Cologne yellow* consists of lead chromate and sulphate, sometimes with calcium sulphate. *Paris yellow* is a mixed 'chrome' of a somewhat similar type. Other products are *primrose chrome*, *pale chrome*, *middle chrome*, and *deep chrome*. These colours are far from permanent, being sensitive to the action of sulphuretted hydrogen, darkened in admixture with sulphide pigments, and liable to change in the presence of reducing substances. For water-colours and distempers, however, tinting, the yellow chromes are useful. In oils, they are permissible, with certain limitations.

*Zinc chrome, Citron yellow*, zinc chromate,  $ZnCrO_4$ , is a pale yellow pigment of fairly good covering power, less used alone than for associating with Prussian blue in the production of various shades of mixed greens. The composition of this pigment is sometimes represented by the formula  $3(ZnCrO_4) \cdot K_2Cr_2O_7$ . Zinc chrome is not affected by sulphuretted hydrogen, and is miscible with most other pigments without deterioration. Acids, alkalis, and organic compounds attack it, the last-named having a tendency to change the colour from yellow to green.

*Lemon chrome, Lemon yellow, Baryta yellow, Barium chrome, permanent yellow, yellow ultramarine, Steinbiller yellow, and Jaune d'Outremer*, are names given to barium chromate,  $BaCrO_4$ , the most stable of the chromium pigments. Prepared by the double decomposition of barium chloride and potassium chromate, filtering, washing, drying, and grinding; lemon yellow is obtained as a very pale, moderately opaque, and serviceable pigment, which can be used with safety in oils and fresco. For water-colour painting it is less suitable, the yellow assuming a greenish hue under unfavourable conditions of exposure. The greatly inferior *strontium yellow*, strontium chromate,  $SrCrO_4$ , is not infrequently substituted for baryta yellow.

*Line chrome*, calcium chromate,  $CaCrO_4$ , is a similar pigment of little value

*Siderin yellow*, basic ferric chromate,  $Fe_2(CrO_4)_3$ , is a somewhat pale-hued product, very stable, useful in stereochemistry (water-glass painting), and of occasional application in water-colour work.

*Copper chromate*  $CuCrO_4$  is a red salt, somewhat dull in hue, which has been proposed and actually used as a pigment, but it is fugitive and of little practical value. The equally unserviceable mercury and silver chromates have already been mentioned (*v. supra*).

*Chrome red, Austrian cinnabar, Orange chrome, Derby red, Chinese red, &c.*, basic lead chromate,  $PbCrO_4$ ,  $PbO$  or  $Pb_2CrO_4(OH)_2$ , is an orange-scarlet pigment, made by heating normal lead chromate with a dilute solution of sodium or potassium hydroxide. The shade obtained depends upon the extent to which the reaction proceeds. Like the yellow chromes, the chrome reds are

liable to change in the presence of reducing substances, such as oxidisable organic pigments. But, unlike the yellows, they may be used with caution in tempera work.

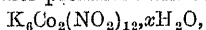
*Chrome green, Vert de chrome, true chrome green.* Prepared by (a) igniting ammonium dichromate, (b) igniting mercurous dichromate, (c) heating together chrome and sulphur, (d) the mixture of potassium dichromate, ammonium chloride, and sodium carbonate. This fine pigment is, or should be, of a pure, anhydrous chromium (or, according to another process of manufacture) chromium phosphate,  $Cr_2(PO_4)_3$ . Some products are a mixture of the two compounds. The oxide pigments are of finer hue than the phosphate colours. Chrome green is one of the most permanent, generally trustworthy, and widely applicable colours used by artists.

*Mixed chrome greens* are mixtures of chrome yellow, barium sulphate or gypsum, and Prussian blue. These are greatly inferior to true chrome green and are unstable in the presence of sulphur, lime, alkalis, and oxidisable vegetable or animal pigments.

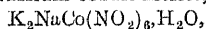
*Viridian, Veridian, Vividian, Guignet's green, Mitter's green, Vert emeraude*, hydrated chromium sesquioxide,  $Cr_2O_3 \cdot 2H_2O$ , is prepared by calcining a mixture of crystallised boric acid with about one-third its weight of potassium dichromate, treating the residue with hot water, washing, wet-grinding, and drying. One of the most valuable pigments used in art, viridian is universally applicable, without action upon other pigments, and absolutely permanent. Though called, in France, *Vert emeraude*, it is, of course, entirely distinct from the fugitive and poisonous emerald green already described among the copper pigments.

**Pigment containing nickel.** *Nickel yellow* is a permanent colour, obtained by precipitating a solution of nickel sulphate with sodium phosphate, washing, drying, and igniting.

**Pigments containing cobalt.** *Cobalt yellow, Aurcolin*, cobalto-potassium nitrite,



or sodium-potassium-cobalt nitrite,



is a bright yellow, durable pigment, which is

without action upon other pigments, with the exception of the lakes, and is only very slowly attacked by sulphuretted hydrogen. Aureolin is permanent in water-colour, as well as in oils.

*Cobalt pink, magnesia-cobalt pink*, is produced when a thin paste of finely divided cobalt carbonate together with an

of cobalt nitrate is dried, and subsequently ignited in a covered vessel at a high temperature. Strongly ignited cobaltous arsenate and phosphate are also of a pink or foxglove-red colour, inclining to violet. These pigments are sometimes known as 'cobalt red' or 'cobalt violet.'

*Rinmann's green, Cobalt green*, sometimes termed *zinc green*, cobalt zincate,  $\text{CoOZnO}$ , is a delicately shaded and artistically satisfactory pigment, of great permanence, and innocuous to other colours. The best product is obtained by drying and calcining zinc oxide, previously made into a paste with an aqueous solution of cobalt nitrate, sulphate or chloride. Another cobalt green is prepared by mixing zinc and cobalt solutions with sodium phosphate, and igniting the washed and dried precipitate. The product so obtained has a bluer tint than the true Rinmann's green.

*Turquoise green, chrome-alumina cobalt oxide*, is a bluish-green pigment mostly used in ceramic painting, but occasionally also in oils. It is made by heating to redness aluminium and chromium hydroxides together with cobaltous carbonate.

*Cobalt blue, Thénard's blue, Leyden blue, King's blue, cobalt ultramarine, Gahn's ultramarine, azure blue, &c.* Several methods are used in the production of cobalt blue. The variety of this pigment known as Wenzel's blue can be prepared by adding ammonia to a solution of cobalt chloride, mixing the precipitated and washed hydroxide with alumina, drying, and igniting; or by moistening recently precipitated aluminium hydroxide with a solution of cobalt nitrate, drying the mixture, and strongly igniting it. Another cobalt blue is made by mixing freshly precipitated and washed cobalt phosphate with newly precipitated and washed aluminium hydroxide. The mass is dried, ignited, and ground. Cobalt arsenate may be substituted for the phosphate. Also a mixture of alum and cobalt nitrate solutions may be precipitated by sodium carbonate, the precipitate being washed, dried, and ignited, as usual. It will be seen that cobalt blue may be a cobalt aluminate or a compound of the phosphate or arsenate of cobalt with alumina.

These cobalt pigments are permanent, except in the presence of ammonium sulphide. They are available in all media, including fresco, and are without action upon other pigments. The tint of the blue is slightly greenish, and in artificial light a shade of violet is perceptible. Cobalt blue is especially valuable in water-colour, for which it is somewhat more suitable than for painting in oils.

*Leitch's blue, or cyanine blue*, is a 'mixed' pigment, composed of cobalt blue and Prussian blue. It is moderately durable, but presents no very striking advantages. As Prussian blue is a constituent, this pigment cannot be used in fresco work.

*Smalt, Saxon blue*, is a silicate, is a deeply coloured gl.

of division, was at one period much used as a pigment. Artificial ultramarine has, to a great extent, replaced it. Smalt is deficient in chromatic and covering power, but it is perfectly durable and without injurious effect upon any other pigments.

*Cœruleum, Cerulean blue, Cœlinblau, Bleu céleste*, cobalt stannate, is a greenish-blue, permanent, semi-opaque colour, made by igniting stannic oxide, previously moistened with a solution of cobaltous nitrate. It possesses the advantage of appearing less violet by artificial light than the other cobalt blues.

*Cobalt brown* results when cobaltous sulphate, ferrous sulphate, and ammonium sulphate, or ammonia alum, are very strongly heated together. Another method of manufacture is to mix ferric oxide with aluminium hydroxide and a cobaltous salt, the mixture being then ignited.

**Pigments containing manganese.** *Manganese green, Cassel green*, barium manganate, is made by cautiously heating a mixture of manganese nitrate or oxide with barium nitrate. Or, manganese dioxide and carbonate may be heated with another manganese green as follows. A solu-

chlorate is precipitated by violet compound produced is washed, dried, mixed with barium hydroxide and carefully heated. A green mass results, which requires washing with water and further treatment.

*Manganese blue.* A mixture of kaolin, manganese oxide and barium nitrate, or of silica, manganese oxide and barium nitrate, ignited at a red heat, is stated to yield a blue product, available for use as a pigment. Soda ash, silica, calcium carbonate, and manganese oxide, mixed together and calcined, yield a similar product.

*Manganese violet, mineral violet, permanent violet*, impure manganese metaphosphate, is prepared by evaporating to dryness a mixture of solutions of phosphoric acid and manganous chloride, fusing the residue, boiling with ammonium carbonate solution, allowing the turbid liquid to stand, filtering, evaporating the filtrate to dryness, fusing the residue, pulverising it and boiling with water. The pigment separates as a fine violet precipitate, which must be collected on a filter, washed, and dried.

*Raw umber, Turkey umber, Levant umber, Terra ombræ*, is a greenish to yellowish-brown, siliceous and ferruginous earth, containing a considerable proportion of one or other of the higher oxides of manganese,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$ . Most of the best specimens are of Cypriot origin, but many countries yield a supply of this natural pigment, which merely has to be ground, levigated, and dried at  $100^\circ$ . Raw umber is a permanent and justly-valued pigment. It has no injurious effect upon other stable colouring matters.

*Burnt umber, Velvet brown, Chestnut brown, &c.*, result from the calcination of raw umber; they are equally permanent, and can be used in conjunction with all other durable pigments. The colour of burnt umber is warmer and richer than that of the raw product.

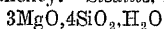
*Cappagh brown, mineral brown, eucchrome*, is a highly manganeseous and ferruginous earth,

**Pinkish-sordid calcium.** *Terra*  
*alba* *liphate*,  
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , is obtained from the crude mineral  
by crushing, levigation, and drying. It is a  
permanent and useful pigment, innocuous to  
other colours and possessed of greater body  
than barytes. Paper stainers and paper-  
makers use it in large quantities. The pigment  
known as satin white usually consists of a  
mixture of calcium sulphate and aluminium  
hydroxide,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . It possesses more body  
and covering power than gypsum alone.

*Whitening*, *white*, *Paris white*, *Spanisch white*, *dust*, *Gilders' white*, *Kreide*, *Craie*, calcium carbonate,  $\text{CaCO}_3$ . This pigment is used as a 'filler' or 'assistant' in mixed paints, but chiefly for whitewashing and in distemper work, as it is permanent and can be used in all pigments, excepting vegetable colours, Prussian blue, emerald green, chrome yellow, and the like, which are likely to be affected adversely by alkalis. In oil, whitening is unservicable and a bad drier.

**Pigments containing magnesium.** *Magnesium carbonate*,  $\text{MgCO}_3$ , prepared from the mineral magnesite by crushing and levigation, has sometimes been used as a pigment. It is permanent and available for admixture with other pigments, excepting such as are injured by alkalis.

**Pigments containing silicon.** *Pure silica*,  $\text{SiO}_2$ , ground to an impalpable powder, is useful for admixture with all pigments, excepting the silicious ochres, its use being that of a reinforcing or inert and pre-eminently permanent pigment for employment as a pigment alone. The main advantages of silica are its 'tooth,' and its absolute permanency. *Sealite*, *Soapstone*,



is used to impart a glaze to some special paints. (For kaolin, *v. Pigments containing aluminium*.)

**Pigments containing, or consisting chiefly of, carbon.** *Soot black*, *vegetable black*, *lampblack*, *smoke black*, *candle black*, *flame black*, *gas black*, *carbon black*. These widely used pigments are soots, obtained by the incomplete combustion of mineral oils, greases, and fat-oils, resins, tarry matters, and natural gas. Carbon or gas black is mostly produced in the combustion of the last-named. *Acetylene black* is an especial variety of gas black, obtained by the combustion together in a cylinder acetylene and a limited supply of oxygen.

derived from tar, naphthalene, pitch, &c.: true lampblack is mainly from liquid raw materials. These pigments are nearly pure carbon, perfectly inert, entirely permanent, and uninjurious to all other colouring matters, with the exception of a few unstable organic compounds, liable to be decolourised by carbon. A very fine, pure lampblack is the pigmentary basis of Chinese or Indian ink.

*Animal black*, *bone black* (*Beinschwarz*), *ivory black*, *Paris black*, *sugar house black*. The first is obtained as the carbonaceous residuum of the destructive distillation of miscellaneous animal offal, the second in a like manner from bones, and the third is or should be produced from waste ivory. Ivory is decolourised when the lime salts have been removed by treatment in hydrochloric acid—is the most intense of the black pigments: it is stated (Toch) that lampblack will make a light mark on ivory black. The animal blacks exert considerable decolourising power when associated in an admixture with other colouring matters.

*Charcoal black*, *Frankfort black*, *German black*, *drop-black*, *blue-black*, *vine-black*, and the like, may shortly be described as charcoals. They are made by calcining in closed vessels materials of the most diverse descriptions, and, as may be expected, vary greatly in value, quality, and cost. The finest bluish-black and velvety products are obtained from vine and beech twigs, fruit stones, coco-nut shell, grape husks, and dried wine-lees. Inferior charcoal blacks result from the charring of very many non-resinous, soft woods. Bass, willow, and maple woods, also paper mills' refuse, are among the materials employed. Drop-black is so named because it is sent into the market in the form of drops, into which it has been mixed with the aid of a little glue-water.

*Mineral black*, *slate black*, *oil black* or *black chalk*, is a brownish-black to blue-black, highly carbonaceous shale, occurring in Bavaria, Spain, Italy and elsewhere, suitable for pigmental use, after crushing and levigation or wet-grinding. *Coal blacks* are somewhat similar. In common with other mineral blacks, *coal black* dries slowly, but is of great permanency. The more intense blacks, of artificial origin, are superseding the different varieties of shale- and coal-blacks.

*Graphite*, *plumbago*, or *black lead* is a dark grey to black pigment, of absolute permanence, available for use with all media, and miscible with other pigments. Nearly pure carbon, and extraordinarily inert, it is a valuable ingredient of paints used as protective coatings for metals. This application of plumbago is exemplified in the familiar stove polishes. With white pigments, graphite supplies the artist with neutral greys. Its use in the manufacture of drawing pencils need merely be mentioned here.

*Prussiate black* is the washed and dried carbonaceous residue, obtained as a bye-product in the manufacture of potassium ferrocyanide.

*Prussian black* results from the calcination of Prussian blue, is a mixture of carbon and oxide of iron, possesses a brownish shade and presents no permanent change of colour.

*Bistre* is a brownish-black pigment, obtained from the smoke of beechwood. It is used by digestion and repeated boiling with water, levigation, and grinding with gum-water or linseed oil, or both. Bistre, which is not used in oils, is somewhat fugitive.

*Bone brown* is prepared by calcining bones until they are of a brownish colour, and grinding the product.

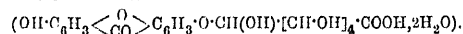
*Vandyke brown*, as generally met with in this country, is a highly discoloured, ferruginous pigment, of a fine, rich hue, this variety is decidedly fugitive, especially in water-colour. Two other, more permanent, but far less richly-tinted pigments, sold under the same name, consist of a brown variety of *caput mortuum*, and a calcined ferruginous ochre, respectively. Imitation Vandyke browns are made, consisting of ochre, colethar, and lampblack, in admixture.

*Cassel brown*, *Rubens' brown*, *Cologne earth*, *Cullen earth*, *coal brown*, and the like are, for the most part, varieties of brown coal or lignite. Some are ochreous in character and approximate in composition to the umbers. These pigments

are subject to such variability of composition, that they cannot safely be trusted for artistic purposes.

*Asphaltum, bitumen, mineral pitch, mummy.* The use of asphalt or native bitumen, as a pigment, has been virtually abandoned by artists, but large quantities from Trinidad and elsewhere are consumed in the manufacture of varnishes, such as Brunswick black, carriage varnish, and black japan. Extreme brittleness is a disadvantageous feature of asphalt coatings. Much of the asphalt used in varnish-making is an imitative product, derived from coal-tar. The use of native bitumen by the ancient Egyptians, for embalming the dead, led to the application, in after-centuries, of the exhumed remains, ground to dust (bitumen, bones and all), as an artists' pigment, under the name of *mummy*. This colour, in an oil vehicle, is more permanent than asphaltum.

**Other pigments of organic origin.** *Indian yellow, Purree, Puri, Purree Arabica*, is composed mainly of the impure, basic magnesium salt of cuxanthic acid



The compound is  $\text{Mg} \cdot \text{C}_{10}\text{H}_{10}\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , and is excreted in the urine of cows fed upon the leaves of the mango tree, *Mangifera indica* (Linn.). This pigment is exclusively made by natives of India at Monghyr, Bengal. The urine is evaporated, the yellow residue dried, collected on calico and rolled into balls, which are sold in the native bazaars. Indian yellow is moderately permanent in oils, well suited for fresco work, somewhat fugitive in water-colour, and apt to injure certain of the lakes when associated with them. It is unaffected by sulphur compounds.

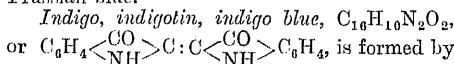
*Gallstone*, a yellow pigment derived from a calculus formed in the gall-bladder of oxen. It has been used as a pigment, but is of no permanence and little value.

*Gamboge, gutti, gummigutti, gomme-gutte.* This familiar pigment is a gum-resin yielded by Malayan, Siamese, Burmese, Indian, and Cingalese species of *Garcinia*. Gambogic or cambogic acid, the principal of the resin acids constituting the pigment, is  $\text{C}_{20}\text{H}_{20}\text{O}_6$  (Buchner). Gamboge is better adapted as an oil pigment than for water-colours, but even in oil it is not permanent unless beeswax, solid paraffin, or a resin such as Venice turpentine or copal be present also. As a water colour, gamboge is best avoided: alkalis darken it, and light not infrequently diminishes its brilliancy of tint. If admixed with cadmium sulphide or barium chromate, it is less alterable, but aureolin and purree are more trustworthy pigments.

*Dragon's blood.* The dragon-tree of the Canary Islands, *Dracæna Draco* (Linn.), the rattan tree, *Calamus draco*, and a variety of other plants, yield deep red-coloured resins known in commerce under the above name. The chief supplies appear to be obtained from *Doemondrops draco* (Blume), and are exported to Europe from Southern and Eastern Asia, under the name of palm dragon's blood. The main tinctorial component consists of the benzoic and benzoyl-acetic esters of dracoresinotannol,  $\text{C}_6\text{H}_5\text{O} \cdot \text{OH}$ , associated together; the first named being greatly in excess. Dragon's blood is mostly used as a colouring ingredient for

varnishes, wood stains, French polish, and the like. As a pigment it is fugitive and untrustworthy. It dries poorly and is injured by certain other pigments, such as flake white.

*Hooker's green and Prussian green* are 'mixed' pigments, composed of gamboge and Prussian blue.



the fermentation of the glucoside, indican,  $\text{C}_{52}\text{H}_{52}\text{N}_2\text{O}_{33}$ , a constituent of various species of *indigofera*, especially *I. tinctoria* (Linn.), and of other plants, such as woad, *Isatis tinctoria* (Linn.). Commercial indigo is impure indigotin and is greatly improved in quality and hue ('intense blue') by successive treatment with hydrochloric acid, hot water, sodium hydroxide solution and strong alcohol (Church). Synthetic indigo is now a formidable rival to the natural product, and is stated to contain 97 p.c. of the pure pigment. Indigo in oils and water is wanting in permanence, and suffers deterioration in the presence of other pigments. It is alleged, however, that there are prepared 'absolutely fast' indigo lakes (Zerr and Rübenkamp, Eng. ed., 1908, translator's note, p. 450).

*Sepia* is the dark brownish-black pigmentary matter contained in the ink-bags of the *sepia*, or cuttlefish, and allied cephalopodous organisms. The method of preparation consists in boiling the crude sepia with caustic soda solution, filtering, precipitating the colouring matter from the alkaline solution by the addition of acetic acid, collecting, washing, and drying. It is permanent, inert, and suitable both for oils and aqueous media. It is a monochrome work and is of a violet tinting. The exact chemical nature of the compound melanin (apparently a weak organic acid, *sepiatic acid*), which constitutes 78 p.c. of the pigment, is at present incompletely studied.

**Pigments composed of lakes.** The lake colours have, during the past two decades, become of prominent importance. They are fully dealt with in the article 'LAKES,' vol. iii. p. 235. In contradistinction to the pigments already described, which, for the most part, are substantive colours, i.e. consist of homogeneous particles (e.g. aureolin, chrome green, lamp-black), the lake pigments are dyestuffs and are compounds of a soluble colouring principle with an insoluble inorganic base, most often metallic, and generally, but not invariably, white. Among the bases employed are aluminium hydroxide, calcium sulphate, zinc oxide, kieselsol, kaolin, and iron oxide, but many others are used. Three classes of lakes come within the category of pigments: (1) lakes made from animal colouring matters; (2) lakes prepared from vegetable substances; and (3) lakes obtained from coal tar products. Lakes belonging to the first two classes were in use at a very early period, but the far more numerous lakes made from artificial colouring principles are of quite modern introduction.

*Carmine* is the most important example of a lake pigment belonging to the first of these classes. The dried females of the cochineal insect, *Coccus cacti*, are boiled with water, alum,

stannous chloride and sodium carbonate being added. After standing for a few days, the decanted liquid throws down the pigment as a crimson precipitate, which is washed and dried. Analysis shows that the major part of the inorganic base present, together with the carminic acid,  $C_{22}H_{22}O_{13}$  (Liebermann), is alumina. By varying the quantity and nature of the base, other lake pigments—cochineal lakes—are produced. These contain more water and more of the aluminous or other bases than carmine. *Carmine lake* (Florentine, Vienna, Paris or Munich lake) may be regarded as little more than a variety of carmine. *Crimson lake* is more basic than either. *Purple lake* contains a lime-alumina base, and *scarlet lake* is a 'mixed' pigment, composed either of alizarin red or of crimson lake, brightened by vermilion.

*Indian purple* results when cochineal extract is precipitated by solution of copper sulphate.

*Burnt or roasted carmine* is obtained by cautiously heating carmine. A similar product, called *burnt lake*, can be prepared from crimson lake.

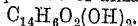
All these lakes, though beautiful in hue, and should be excluded from the artist's palette.

*Lac lake, Indian lake, lac dye lake, lack lack.*

A resin called gum lac is formed on *Ficus* (punctured).

to the cochineal, though initially vegetable, runs from the female insect and solidifies on the twigs as stick lac. This, extracted with water, yields lac dye, and the insoluble residue constitutes the seed lac and shellac of commerce. After purification, the lac dye (laccic acid,  $C_{16}H_{12}O_8$ , Schmidt) is extracted with an alkaline solution and subsequently treated with alum. The precipitated lac lake is washed and dried. This pigment is less fugitive than the cochineal lakes, but its hue is inferior (v. LAC DYE).

Among the lake pigments belonging to the second class mentioned above, those prepared from vegetable substances, are the natural madder lakes. The madder root, *Rubia tinctorum* (Linn.), contains, together with purpurin,  $C_{14}H_5O_2(OH)_2$ , the glucoside ruberythric acid,  $C_{26}H_{22}O_{14}$ , which by hydrolysis yields dihydroxy-anthraquinone or alizarin,



This compound is capable of giving, according to the nature and proportions of the bases employed in association with the acidified and washed madder root (alumina, lime-alumina, iron oxide, copper oxide, *et alia*), crimson, pink, purple, brown, and plum-coloured lakes. Under similar conditions, purpurin gives orange-hued and bright-red products. The madder pigments are madder, madder carmine, pink madder, purple madder, Rubens' madder, and madder brown; but these lakes from the madder root are now almost obsolete, the madder root being replaced by artificial alizarin and purpurin.

$C_{14}H_{10}$ , having led to the cheap and facile production of artificial 'madder lakes' (*infra*) on a large commercial scale. Whether natural or of artificial origin, the madder pigments, although alterable by prolonged exposure, are, as a class, far less perishable than the cocculus lakes. This statement does

not apply to the so-called 'yellow madder,' yellow lake (ne ... the like, which are extremely

Other lakes ... sources are those from red sanders wood, alkanet root, *Anchusa tinctoria* (Lam.) (including the pigment called violet carmine), Brazilwood, logwood or campeachy wood, archil, buckthorn, and quercitron or black oak. The pigments known as Vienna lake and rose pink are prepared from Brazil wood, *Caesalpinia Braziliensis* (Linn.); yellow lake, brown pink, Italian pink, 'yellow madder,' Dutch pink, yellow carmine, citrine lake, 'stil de grain,' sap green, lokao (Chinese green), and quercitron bark, from different

species of buckthorn (*Rhamnus*), including Persian, Avignon and other berries. Violet, blue, red, and intense blue-black lakes can be prepared from logwood. *Hematoxylon campechianum* (Linn.). French purple is an archil lake. Red and violet lakes are yielded by red sanders or santal wood, *Pterocarpus santalinus* (Linn.). All these pigments are fugitive and untrustworthy. Old fustic, *Chlorophora tinctoria* (Gaudich), young fustic, *Rhus Cotinus* (Linn.), and turmeric, *Curcuma tinctoria*, may be mentioned here, but they are dye-woods, rather than sources of pigments (v. separate articles).

There remain to be considered the lakes obtained from coal-tar products. These, to a great extent, have superseded the lakes of animal and vegetable origin. They have already been described in the article 'LAKES' to which reference may be made. The following short list includes only some of the names of these lakes (Group

1. Alizarin or artificial madder lakes (previously mentioned); the names of some of the pigments have already been given, but the commercial designations of other representative examples are alizarin orange (marigold, pure yellow), alizarin carmine, permanent crimson, olive green, olive lake, sap green, Indian lake, scarlet lake, alizarin pink, alizarin blue, and alizarin violet.

Group 2. The triphenylmethane,  $CH(C_6H_5)_3$ , or rosaniline group of lakes: e.g. the magenta and violet lakes. Group 3. Lakes from the halogen-substituted phenol-phthaleins, or eosins; e.g. 'vermillionettes,' Victoria reds, Royal reds, &c.

Group 4. Lakes from the rhodamines: e.g. deep pink

Group 5. Lakes from ... exceedingly nu

from various shades of yellow to deep violet-reds. Group 6. The azine, oxyazine, and thioazine lakes: e.g. Nile blue A, methylene blue B; also various red lakes.

Unfortunately, the pigments obtained from the artificial colouring matters, with the exception of the alizarin lakes and some of the pigments produced from the azo colours, are neither light-fast nor are they damp-fast or air-fast. Many of the most brilliant products are deteriorated by a few hours' exposure. Apart from the artificial madder lakes, practically all these exquisite pigments are useless to the artist.

**Stability.** For many years past much attention has been devoted to the subject of the permanency or stability of pigments under

various conditions. The agencies to which the painter's colours may ordinarily be subjected are light, air (possibly in association with varying quantities of noxious gases, such as sulphuretted hydrogen and sulphur dioxide), moisture, the vehicle or medium used, the associated pigments, and, in some cases, the painting ground.

As long ago as 1772, Sir Joshua Reynolds tested some of the pigments he used, and since his time many observers have similarly experimented, but in a more systematic and scientific manner: among them, Decaux, Simpson, Rood, and Abney, Church and Laurie. Much good work in this connection has been done by the Munich Deutsche Gesellschaft für Beförderung rationeller Malverfahen; and during the years 1894-1904, the Burlington Fine Arts Club carried out a series of valuable tests of water-colour paints, exposed to light under different conditions. Ogden N. Rood, whose experiments were made with washes of several dozen water-colours upon drawing-paper during three and a half summer months' exposure, found only the following twelve pigments unaffected: yellow ochre, Roman ochre, cadmium yellow, Indian red, light red, *jaune de Mars*, cobalt, smalt, French blue, burnt sienna, burnt umber, and terre verte. The experiments of Russell and Abney, upon the action of light on water-colours, showed that when washes upon Whatman paper were exposed for nearly two years to light and air, the following pigments remained unchanged: Indian red, Venetian red, burnt sienna, chrome yellow, lemon yellow, raw sienna, terre verte, chromium oxide, Prussian blue, cobalt blue, French blue and ultramarine ash. In the table below, the approximate order of instability of the pigments, the most fugitive being placed first, is set forth:—

1.*Carmine	16.*Violet carmine	28. Indian red
2.*Crimson lake	17.*Purple carmine	29. Venetian red
3.*Purplemadder	18.*Sepia	30. Burnt sienna
4.*Scarlet lake	19. Aureolin	31. Chrome yellow
5.*Payne's grey	20. Rose madder	32. Lemon yellow
6.*Naples yellow	21. Permanent blue	33. Raw sienna
7.*Olive green	22. Antwerp blue	34. Terre verte
8.*Indigo	23. Madder lake	35. Chromium oxide
9.*Brownmadder	24. Vermillion	36. Prussian blue
10.*" "	25. Emerald-green	37. Cobalt blue
11.*" "	26. Burnt umber	38. French blue
12.*" "	27. Yellow ochre	39. Ultramarine ash
13.*Indian yellow		
14. Cadmium yellow		
15. Leitch's blue		

The colours marked with an asterisk altered during only four months' exposure; Nos. 27 to 39 showed no change during two years. Of thirty-four mixtures, only three remained unaltered at the end of the period; but six mixtures containing Prussian blue, though changed at first, returned more or less to their original colour when kept in the dark for six weeks. Prussian blue, which has suffered in tint from exposure, is well known to possess the power of recovering its colour when placed in darkness. Among Russell and Abney's conclusions were: (1) that mineral colours are far more stable than vegetable pigments; (2) that moisture and oxygen are essential for changes to be effected in vegetable colours; (3) that in a mixture of colours having no direct chemical action on one

another, light causes the unstable colour to fade, leaving the stable pigment virtually unaltered; and (4) that the more refrangible rays of light, which produce the most rapid fading in pigments, are present in small proportion in the lights in illuminating a room or picture-gallery.

The German society above-mentioned selected the following list of *normal colours* for oil-painting, as having been shown by experience to be the most permanent and trustworthy under the influences of light and air: white lead, zinc white, Naples yellow, cadmium yellow (darker shades), Indian yellow, brown and yellow ochre, terra di siena, burnt ochre, red ferric oxide colours, vermilion, madder (alizarin) lake, cobalt blue and green, ultramarine, the Prussian blues, chromium oxide green, green earth, umber, asphalt, mummy, ivory black and lampblack (Zerr and Rübenkamp).

The Burlington Fine Arts Club trials, which were made with washes of a considerable number of moist water-colours upon Whatman paper exposed to dry air, moist air, and in glazed frames, were totally unfavourable to yellow, Vandyke brown, crimson lake and vermilion; but it was proved that Prussian blue, indigo, sepia and other pigments liable to change in damp air, may be regarded as tolerably stable if so framed as to be kept dry.

As the outcome of many experiments of his own and a consideration of the results obtained by other observers, Church concluded that, for oil-painting, the following pigments are truly permanent:—

Flake white	Vermilion	Cobalt
Zinc white	Cobalt violet	Cornelium
Baryta white	Manganese violet	Burnt sienna
Yellow ochre	Emerald oxide of chromium	Raw and burnt umber
Raw sienna	Green oxide of chromium	Verona brown
Naples yellow	Green ultramarine	Cappagh brown
Cadmium yellow	Cobalt green	Prussian brown
Cadmium orange	Ultra-natural	Ivory black
Red ochre	marine	Charcoal black
Venetian red	Ultra-artificial	Lamp black
Light red		Graphite
Indian red		

Generally allowable, though liable to some alteration in special circumstances, are—

Baryta yellow	Madder red	Prussian blue
Strontia yellow	" carmine	Antwerp "
Chrome yellow	Mars violet	Madder brown
Aureolin	Emerald green	Vandyke brown
Indian yellow	Madder green	(earthy)
Rose madder	Malachite green	Cologne earth
Purple madder	Terre verte	Bitumen
Rubens' madder	Smalt	

And the pigments named below, in Church's opinion, should not be used in artistic painting:—

Yellow madder	Crimson lake	Green vermilion,
Brown pink	Indian lake	etc.
Yellow lake	Purple "	Indigo
Gamboge	Scarlet "	Blue verditer
King's yellow	Violet carmine	Blue ochre
Zinc chromate	Sap green	Vandyke brown
Carmine and burnt carmine	Verdigris	(bituminous)

For water-colour and tempera painting, flake white, pale cadmium, true Naples yellow, chrome yellow, artificial vermilion, malachite green, madder brown, bistre, and sepia, must be added to this last list as being quite untrustworthy. Other pigments, in addition to the foregoing, are unsuitable for fresco work and stereochromy e.g. the Prussian blues,



Antwerp blue, all the chromates and the madder colours.

The pigments regarded by Decaux as quite unchangeable in oils are: zinc white, flake white, yellow ochre, Naples yellow, deep cadmium, raw sienna, red ochre, Mars red, Venetian red, burnt Italian earth, green oxide of chromium, terre verte, green ultramarine, artificial ultramarine, cobalt blue, and ivory black.

With reference to the action of foul gases, it may be stated generally that the lead and copper pigments are especially sensitive to sulphuretted hydrogen; the chromates of zinc and barium are liable to turn green in the presence of sulphur dioxide; ammoniacal vapours will injuriously affect the copper greens and Prussian blues; acid fumes may injure ultramarine, and reducing or oxidising gases attack indigo.

Certain pigments should not be used in conjunction: thus, aureolin and indigo, aureolin and cochineal lakes, cadmium yellow and emerald green, vermilion and malachite, white lead and lithopone, and chrome yellow and lithopone, are examples of mixtures, the components of which may mutually react when intimately mixed. In an oil medium, there is less likelihood of such injurious interaction than with water-colour pigments, but it may be affirmed that it is in general wiser to mix pigments on the palette than to grind them together.

E. G. C.

**PILOCARPENE, PILOCARPIDINE, PILOCARPINE** *v.* JABORANDI.

**PILOLITE** *v.* ASBESTOS.

**PIMARIC ACID** *v.* RESINS.

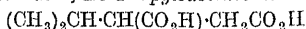
**PIMELIC ACID**  $C_6H_{10}O_4$ . Twenty-five isomeric acids having this formula have been prepared, and of these three are known as *pimelic acid*.

*Normal pimelic acid*  $CO_2H[CH_2]_4CO_2H$ , obtained by the oxidation of fats (Bouveault, Bull. Soc. chim. 1898 [iii.] 19, 562), and of castor oil (Gantter and Hell, Ber. 1884, 2213); prepared by the oxidation of suberone (*v.* suberic acid) with nitric acid (Schorlemmer and Dale, Annalen, 199, 147); by heating pentanetetra-carboxylic acid at  $200^\circ-220^\circ$  (Perkin and Prentice, Chem. Soc. Trans. 1891, 825); by treating *ac*-dichloro-, dibromo-, or di-iodopentane with potassium cyanide and hydrolysing the nitrile thus formed (Braun, Ber. 1904, 3588; Hamonet, Compt. rend. 1904, 139, 59); by the interaction of the sodium compound of ethylcyanacetate and trimethylene dibromide (Carpenter and Perkin, Chem. Soc. Trans. 1899, 924); by the interaction of ethylcyanogen bromide, and phosphor trichloride (Braun, Chem. Zentr. 1909, ii. 111); by the action of sodium in amyl alcohol on salicylic acid (Einhorn and Wilstätter, Ber. 1894, 33; Einhorn and Lumsden, Annalen, 286, 260; Walker and Lumsden, Chem. Soc. Trans. 1901, 1198); by the reduction of furonic acid with hydriodic acid and red phosphorus (Baeyer, Ber. 1877, 1358); by the reduction of piperylene dicarboxylic acid with sodium in alkaline solution (Willstätter, Ber. 1898, 1550); by the interaction of trimethylene bromide and malonic ester and heating the product thus formed (Perkin, *ibid.* 1884, 3289). Crystallises in needles from benzene and plates from water; m.p.  $105^\circ$ .

By heating the acid with lime, *cyclohexanone* is produced. Substituted alkyl pimelic acids are produced by the reduction of substituted *o*-phenol carboxylic acids (Einhorn, Annalen, 295, 173; Chem. Zentr. 1897, i. 1006; D. R. P. 90556).

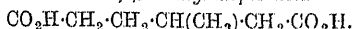
*$\beta$ -pimelic acid* is identical with *normal pimelic acid*.

*Pimelic acid, iso-Propylsuccinic acid*—



prepared by fusing *d*-camphoric acid with caustic alkali (Hlasiwetz and Grabowski, Annalen, 145, 207; Mahla and Tiemann, Ber. 1895, 2152; Crossley and Perkin, Chem. Soc. Trans. 1898, 22); by the action of nitric acid on  *$\beta$ -isopropyl- $\delta$ -ketohehoic acid* (Crossley, Chem. Soc. Trans. 1902, 676); by the action of potassium permanganate on tetrahydrocarvone in alkaline solution (Oehler, Ber. 1896, 36); by treating amylene bromide with potassium cyanide and hydrolysing the resulting nitrile (Auwers and Mayer, Annalen, 298, 150 and 177); by similarly treating *isocapro*lactone (Blaise, Compt. rend. 124, 90); by the reduction of tetranoic acid, dimethyl-4-citraconic acid, or *mesaconic acid* with sodium amalgam (Pittig and Krafft, Annalen, 304, 206); by treating *isothujone* with potassium permanganate and sodium hypobromite (Wallach, Ber. 1897, 423). M.p.  $116^\circ-117^\circ$  (Bentley, Perkin, and Thorpe, Chem. Soc. Trans. 1896, 274); readily soluble in chloroform, benzene, and warm water. Oxidation with potassium dichromate and sulphuric acid converts it into terebic acid,  $C_{10}H_{16}O_4$  (Lawrence, Chem. Soc. Trans. 1899, 527).

*$\gamma$ -Pimelic acid,  $\beta$ -methyladipic acid*—



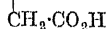
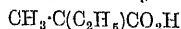
This acid contains an asymmetric carbon atom, and hence exists in two stereoisomeric forms.

*d*-*Acid*, prepared by the oxidation of citronellal or citronellie acid (Tiemann and Schmidt, Ber. 1896, 908; Semmler, *ibid.* 1893, 2257), of *isopulegol* (T. and S., *ibid.* 1897, 25), of *pulegone* (Semmler, *ibid.* 1892, 3516), or of *menthone* (Manasse and Rupe, *ibid.* 1894, 908). Can be obtained from menthol (Beckmann and Mehrländer, Annalen, 289, 378). Melts at  $93^\circ-94.5^\circ$  (Wagner, Ber. 1894, 1642), at  $84.5^\circ$  (Semmler, *l.c.*).

*l*-*Acid*, prepared by the oxidation of *l*-citronellal (T. & S. Ber. 1896, 923), m.p.  $84.5^\circ$ .

*Inactive acid*. Prepared by the oxidation of *i*-citronellal (T. & S. *ibid.* 1896, 925) or from equal quantities of the *d*- and *l*-acids: m.p.  $93^\circ-94^\circ$ .

*isoPimelic acid,  $\alpha\alpha$ -methylsuccinic acid*



prepared from amylene bromide and potassium cyanide (Hell, Ber. 1891, 1390; Bauer and Schuler, J. 1878, 733), or from the mixture of tricarboxylic acid esters (b.p.  $135^\circ-160^\circ$  at 0.15 mm.), obtained by treating ethyl  $\alpha$ -bromo-methylethyl acetate with sodiummalonic ester in xylene solution (Auwers and Fritzweiler, Annalen, 298, 166; 292, 154, and 182): m.p.  $103^\circ-104^\circ$ .

**PIMENTHOL** *v.* CAMPHORS.

**PIMENTO.** Pimento or Allspice is the fruit of *Persea* but unripe fruit of *Pimenta*

The plant is indigenous to the West Indies and is largely cultivated in Jamaica, whence our supplies are derived. The globular berries, dark purple when fresh, brown when dry, are from 5 to 8 mm. in diameter. They are enclosed in a two- but sometimes one- or three-celled fruit. They are gathered when of full size but still not quite ripe, and dried in the sun.

The characteristic flavour is due to an aromatic, pungent, volatile oil, resembling in smell that of cloves; other important constituents being a fixed oil, tannin, resin, and much starch. Full analyses by Richardson (U. S. Dept. of Agric., Div. of Chem. Bull. 13, 221) yielded the following results:—

	Whole	Ground	
	Max.	Min.	
Water . . . . .	6.19	8.82	5.51
Ash . . . . .	4.01	5.53	3.45
Volatile oil . . . . .	5.15	3.32	2.07
Fixed oil . . . . .	6.15	6.92	3.77
Fibre . . . . .	14.83	18.98	13.45
Proteid . . . . .	4.38	5.42	4.03
Nitrogen . . . . .	0.70	0.87	0.64
Quercitannic acid (* tannin equivalent *)	10.97	12.74	8.27

**Uses.** Pimento finds its chief use as a condiment, but it is *officinal* in the British Pharmacopoeia together with an *aqua* and the essential oil. Its therapeutic action is that of an aromatic stimulant and carminative.

**Adulteration.** Comparatively little is sold in the ground state in this country, so that pimento is rarely if ever adulterated here. Very few samples, however, are examined under the Sale of Food and Drugs Acts. The usual spice adulterants may be looked for, namely, added starches, ground olive stones, and the shells of coconut and almond, &c.

**Analysis.** Microscopical examination will suffice to detect all the likely adulterants of vegetable origin. The most characteristic structures to be observed are minute starch grains, usually about  $8\mu$  in diameter and not exceeding  $12\mu$ , with a distinct hilum, often joined in pairs or triplets, or larger aggregates: numerous colourless stone cells, some very large; and pigment cells containing irregular port wine or amber-coloured masses of resin or gum.

The most useful determinations are ash, tannin, and fixed ether extract. Unless adulteration is discovered by the microscope, anything further is seldom required. Should olive stones or nutmeg be suspected of being present, their special characters are given under **PEPPER** (*q.v.*).

The direct determination of tannin is neither easy nor satisfactory, but very fair results may be obtained by calculating the quercitannic acid from the proportion of oxygen absorbed from potassium permanganate.

The process, due to Richardson (U. S. Dept. of Agric., Div. of Chem. 13, 167), is as follows: Boil 2 grms. of the sample, after thoroughly extracting with ether, with 300 c.c. of water for 2 hours, cool, make up to 500 c.c. with water and filter. Mix 25 c.c. of the filtrate with 750 c.c. of water, add 25 c.c. of indigo solution (made by dissolving 6 grms. of potassium sulphindigotate in hot water, cooling, adding

50 c.c. of sulphuric acid (conc.) and making up to 1 litre). Then titrate with the permanganate solution (1.333 grms. per litre) until the liquid becomes of a bright yellow colour. Note the number of c.c. used. Ascertain the equivalent of the permanganate in terms of N/10 oxalic acid and calculate the number of c.c. of the former used in oxidising the pimento solution. Convert this into its equivalent number of c.c. of oxalic acid. Each c.c. of the oxalic acid = 0.0623 gm. of quercitannic acid.

The following table will afford some idea of the figures yielded by genuine samples, but comparatively few analyses of authentic specimens are on record.

Analyses by Winton, Ogden and Mitchell, Ann. Rep. Connect. Agric. Station, 1898, p. 204.

	Max.	Min.	Average
Moisture . . . . .	10.14	9.45	9.78
Ash . . . . .	4.76	4.15	4.47
„ soluble in water . . . . .	2.69	2.29	2.47
„ insol. HCl . . . . .	0.06	0.00	0.03
Ether extract, volatile . . . . .	5.21	3.38	4.06
„ „ fixed . . . . .	7.72	4.35	5.84
Alcohol extract . . . . .	14.27	7.39	11.79
Starch (diastase method) . . . . .	3.76	1.82	3.04
Fibre . . . . .	23.98	20.46	22.39
N. . . . .	1.02	0.83	0.92
Quercitannic acid . . . . .	12.48	8.06	9.71

**Standards.** The United States standard for Allspice provides that the quercitannic acid shall not be less than 8 p.c., the ash not more than 6 p.c., the ash insoluble in HCl not more than 0.5 p.c. and the fibre (which should be determined as in pepper) (*q.v.*) not more than 25 p.c. C. H. C.

#### PIMENTO OIL *v.* OILS, ESSENTIAL.

**PINACHROMY** and **PINATYPE.** Processes of colour photography devised by E. Koenig (v. J. Soc. Chem. Ind. 1906, 657).

**PINCHBECK.** An alloy of zinc and copper brought into notice by Christopher Pinchbeck in the latter part of last century. It was formerly much employed in the making of watch-cases, and other small ornamental articles in imitation of gold. Its composition is variable, but usually consists of 9 parts of copper to 1 part zinc.

**PINE-APPLE.** The fruit of *Ananas sativus* (Schult.) [*Bromelia ananas*] a tropical plant, grown largely in the West Indies, Singapore, Florida, the Bahamas, Natal, and other hot countries. According to Munson and Tolman (J. Amer. Chem. Soc. 1903, 25, [iii.] 272), the average composition (38 samples) of fresh pine-apples, 21 from Florida, 10 from Cuba, 4 from Porto Rico, 2 from the Bahamas, and 1 from Jamaica, is

Pro-	Free acid	Reducing Cane	Insoluble
Water	ten (as $\text{H}_2\text{SO}_4$ )	sugar	sugar
85.83	0.42	0.60	3.91
			7.59
			0.40
			1.52

In different specimens, the reducing sugars varied from 1.75 to 9.75 p.c.; the cane sugar from 3.0 to 10.5 p.c. According to Lindet (Bull. Soc. chim. 1884, 40, 65), pine-apples contain 1 p.c. or more of mannitol. Pine-apple juice is said to contain an enzyme, *bromelain*, which resembles pepsin and can digest a thousand times its weight of proteids in a few hours. It can be precipitated from the juice by the addition of common salt, and can operate in acid,

neutral or alkaline media (J. Franklin Inst. 1902, 154, [iv.] 262). The leaves of the plant furnish a fibre which can be used for the manufacture of rope, being stronger than flax. It is also used in the Philippines for the preparation of a cloth (Board of Trade Journal, Dec. 1898, 671; also Bull. Imp. Inst. 1904, 2, 168). Pine-apples are often canned, being preserved in their own saccharine juice, with or without the addition of sugar. Analyses of commercial samples by Munson and Tolman (*l.c.*) gave the following average figures:—

	Water	Pro-tein	Free acid	Reduc- ing cane sugar	Insol. Ash mat.
I. Singapore	86.73	0.46	0.42	8.00	5.40
II. Singapore	81.83	0.41	0.32	11.63	5.14
III. Singapore and Straits	78.97	0.46	0.26	9.91	7.77
IV. Bahamas	85.87	0.33	0.56	7.96	2.78
				0.38	1.39

I. average of 10 samples known to be preserved in their own juice; II. preserved with addition of cane sugar; III. and IV. commercial samples, III. apparently containing added sugar, IV. probably without added sugar.

The flavour of pine-apples can be imitated by a solution of ethyl butyrate in alcohol (Hofman, Annalen, 81, 87).

**PINE-NEEDLE OIL** *v.* OILS, ESSENTIAL.

**PINE OIL** *v.* OILS, ESSENTIAL.

**PINE RESIN** *v.* RESINS.

**PINUS SYLVESTRIS OIL** *v.* OILS, ESSENTIAL.

**PIPE-CLAY** *v.* CLAY.

**PIPERAZINE** (*Ethylene-imine*; *Diethylene-diamine*), also known as *Dispermine* or *Arthriticine* ( $C_2H_5NH$ )<sub>2</sub>, was first obtained pure by Magert and Schmidt in 1890.

Ammonia is allowed to act upon ethylene bromide or chloride when a mixture of bases is formed consisting of ethylene- and triethylene-diamine, diethylene- and tetraethylene-triamine and diethylene diamine. The last-named is separated from the other salts by treating the mixture with excess of sodium or potassium nitrite and heating to 60°-70°. Dinitrosopiperazine, m.p. 154°, separates as a scaly crystalline mass readily soluble in hot water. The nitroso compound on being treated with concentrated acids or reducing agents yields ammonia and salts of nitrous acid, which the pure base is with alkalis.

Piperazine and its salts are also manufactured by treating ethylene diamine with 40 p.c. aqueous acid sulphite or with hydrochloric, sulphuric, or phosphoric acids. The mixture is heated to boiling, when a violent reaction takes place, and the dinitroso-compound dissolves to a yellow liquid. When the reaction is over, the product is acidified with hydrochloric acid and the amino-phenol-sulphonic acid which separates is filtered off. The filtrate is now made alkaline and the piperazine is distilled off with steam. It is purified by conversion into its hydrochloride and the piperazine is isolated by the decomposition of the latter (Eng. Pat. 5320, 1497; J. Soc. Chem. Ind. 1893, 463; *ibid.* 1894, 275). It is also obtained by the reduction of ethylene oxamide with zinc dust or sodium (D. R. P. 66461); by heating disulphone piperazides with sulphuric acid at 200°-250° and subsequently

treating the product so obtained with powdered sodium hydroxide (Eng. Pat. 7120; J. Soc. Chem. Ind. 1893, 545; D. R. P. 100232); by the decomposition of dibenzyl-piperazine with dilute sulphuric acid at 100° (D. R. P. 98031; Chem. Zentr. 1898, ii. 743); by heating sodium ethylene glycolate with acid derivatives of ethylene diamines at 250°-350° (D. R. P. 67811), and by heating  $\alpha$ - or  $\beta$ -dinaphthyl piperazine with acids or with solutions of calcium or zinc chloride (D. R. P. 79121). For other methods of preparing piperazine, compare D. R. PP. 73354, 70055; 70056; 73125; 74628; 60547; 63618; 65347; 71576; 77351; 83524; 59222.

**Properties.** Piperazine forms lustrous glassy tablets, m.p. 104°; b.p. 140°-145°; readily soluble in water but less so in alcohol. It is very hygroscopic, forming  $C_4H_{10}N_2 \cdot 6H_2O$ , m.p. 44°, b.p. ... on distillation above 135°, yields the pure anhydrous base (Berthelot, Compt. rend. 1899, 129, 687; see also Magert and Schmidt, Chem. Soc. Proc. 1893, 35).

Piperazine readily absorbs carbon dioxide, forming the compound  $C_4H_{10}N_2O_2$  (Roslalsky, J. pr. Chem. 1896, [ii.] 53, 19). Piperazine is a strong base forming crystalline salts with acids of the type  $C_4H_{10}N_2 \cdot 2A$  (Herz, Ber. 1897, 30, 1584).

It is precipitated by mercuric solution, copper sulphate, picric acid, potassium bismuth iodide, and by gold and platonic chlorides. It also combines with bismuth chloride (Yanino and Hartl, Arch. Pharm. 244, 216). In its chemical and physical properties it is very similar to spermine with which it was at one time thought to be identical. Piperazine is readily oxidised by potassium permanganate in the cold; it is non-poisonous and has no caustic action, and owing to the ease with which it forms a readily soluble urate, it is employed in gout and similar manifestations of uric acid diathesis (Riesenthal, Virchow's Archiv. 137, 51; Ber. 1891, 24, 241; 1897, 30, 1584). It is also used for the relief of irritation of the bladder due to excess of uric acid in the urine. Piperazine can be identified in urine by its characteristic lemon yellow picrate (Riesenthal, Chem. Zentr. 1893, ii. 624) or by adding a slight excess of caustic soda, heating the solution, cooling, and filtering. The filtrate is acidified with hydrochloric acid and potassium bismuth iodide is added when a brick red precipitate consisting of characteristic microscopic crystals separates.

Piperazine is best preserved in a solution of 20 parts alcohol and 80 parts water. Like piperidine, piperazine reacts with isatin, forming blue additive compounds (Liebermann and Kraus, Ber. 1907, 40, 2492). It also forms additive compounds with quinols and phenols (Stevenson, Bull. Soc. chim. 1910, [iv.] 7, 922) and with aldehydes, carbon disulphide and carbonyl chloride (Herz, *l.c.*).

Piperazine combines with diiodo-, or dibromo-pentane when they are heated together on the water-bath forming diethylene dipiperidyl halide (Braun, Ber. 1907, 40, 2935).

**n-Dibromopiperazine** is obtained by the action of hypobromous acid on piperazine and treating the product with dilute alkali or piperazine. It forms yellow, transparent short

prisms which, without melting, are dangerously explosive at 79°-80°. It readily combines with two molecules of acid to form a comparatively stable compound which

explodes at 72° without melting (Chattaway and Lewis, Chem. Soc. Trans. 1905, 951). Periodides have been obtained by Linarix, J. Pharm. Chim. 1909, [vi.] 30, 241.

**a-2:5-Dimethyl piperazine**, m.p. 118°-119°, b.p. 162°, is formed by the reduction of 2:5 dimethyl lactimide with sodium and Zeitsch. physiol. Chem. 34, 347; or it is isolated from commercial amyl alcohol by treating it with sodium (Bamberger and Einhorn, Ber. 1897, 30, 226). It is alkaline, readily soluble in water and in alcohol, and sublimes at ordinary temperatures. The  $\beta$ -compound has m.p. 114°.

**a-Dimethylpiperazine tartrate** or **Lycetol**,  $C_6H_{14}N_2 \cdot C_4H_4O_6$ , m.p. 250°, is a white crystalline powder having an acid reaction. It is readily soluble in water, is less hygroscopic than piperazine, and its solution is more stable than that of the latter. It also has a more agreeable taste than piperazine itself.

**Piperazine benzoate**, glistening plates, subliming at 120°, and the **salicylate**, fine white needles subliming at 160°, are formed by mixing alcoholic solutions of the base and acid. The former is alkaline and the latter neutral to helianthin but both are acid to litmus (Astruc, Bull. Soc. chim. 1906). They can also be formed by fusing the two substances together and recrystallising from the above solvent (Eng. Pat. 25905; J. Soc. Chem. Ind. 1897, 933; Pharm. Zeit. 43, 319).

The **tartrate** and **citrate** (Eng. Pat. 26078; J. Soc. Chem. Ind. 1898, 68) which are non-hygroscopic and may be dried at a high temperature, and also the **quinates** (Eng. Pat. 11420; J. Soc. Chem. Ind. 1899, 856) are produced similarly. Piperazine also forms acid salts with oxalic, tartaric and citric acids which yield useful neutral double salts with lithium (Eng. Pat. 18981; J. Soc. Chem. Ind. 1896, 758).

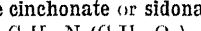
**Piperazine mercuric citrate** is formed by mixing together piperazine and mercuric citrate in absolute alcohol. It crystallises in white needles sintering at 110°, m.p. 137°, and forms a strongly alkaline solution in water.

**Piperazine mercuric acetate** is formed similarly, is fairly soluble in water, darkens at 188° and has m.p. 198°.

Both these salts, as also the corresponding **benzoate** (m.p. 144°-145°), **benzoate** (m.p. 107°-108°), **salicylate** and **nitrate** and also the corresponding **dimethylpiperazine mercuric nitrate** (m.p. 118°-119°), **sulphate** (m.p. 124°-125°), **cyanide** (m.p. 159°-160°), **succinate** (m.p. 108°-110°) and **salicylate** (m.p. 128°-130°) have antiseptic properties and do not coagulate albumen. They can also be prepared by treating the mercuric salt with the carbonate of the organic base (D. R. P. 125095, 1902).

**Piperazine theophylline** is formed by combining molecular proportions of its components or their salts. It has an alkaline reaction, is sparingly soluble in alcohol but readily so in water (D. R. PP. 214376, 217620, 224981; J. Soc. Chem. Ind. 1910, 1134).

**Piperazine cinchonate** or **sidalon**,



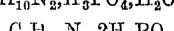
m.p. 168°-171°, is a colourless crystalline powder having an acid taste and reaction and is readily soluble in water (Pharm. Zeit. 45, 182).

**a-Piperazine anthraquinone**, formed by the action of nitroanthraquinone on the base, separates from methyl alcohol in orange-red crystals (D. R. PP. 136777, 136778, 1903).

**Nitrosopiperazine**  $C_4H_8N_2(NO)_2$  formed by adding sodium nitrite to a solution of piperazine hydrochloride and warming the mixture; it crystallises from water in yellowish lustrous plates, m.p. 158°, and gives the Liebermann reaction with phenol and sulphuric acid.

**Diphenyl piperazine**, m.p. 163-5°, is formed by the action of ethylene bromide on aniline, sufficient dry sodium carbonate or acetate being added to fix the hydrogen bromide produced. It combines with a number of diazo and diazo-sulphonic compounds yielding yellow-red and violet dyes for cotton, wool, and silk (Bischoff, Ber. 1889, 22, 1777).

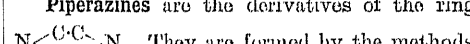
Piperazine forms phosphates and arsenates of the type  $C_4H_{10}N_2 \cdot H_3PO_4 \cdot H_2O$ ;



(Astruc and Brenta, Bull. Soc. chim. 1908, [iv.] 3, 963), and also glycerophosphates (Astruc, Compt. rend. 1906, 140, 727).

A large number of other piperazine derivatives have been prepared (Ladenburg, Ber. 1891, 24, 2400; Bischoff and Nastvogel, *ibid.* 1889, 22, 1783, 1792; Bischoff and Trapesonjanz, *ibid.* 1892, 25, 2940; Wolff, *ibid.* 1893, 26, 721; Herz, l.c.; Stoehr, J. pr. Chem. [ii.] 47, 439; *ibid.* 48, 191; Cazeneuve and Moreau, Compt. rend. 1897, 125, 1182; *ibid.* 1898, 126, 1802; Rijn, Chem. Zentr. 1898, i. 380; Knorr, Ber. 1904, 37, 3507; *ibid.* 1905, 38, 3136; *ibid.* 1906, 39, 1420; Astruc, Bull. Soc. chim. 1905, [iii.] 33, 839; Borsche and Tittsingh, Ber. 1907, 40, 5008; Van Dorp, Rec. trav. chim. 1909, 28, 18; Franchimont, *ibid.* 1910, [ii.] 14, 296).

**Piperazines** are the derivatives of the ring



given above and also by the reduction of the **pyrazines** with sodium and alcohol. They are strong colourless bases, some liquid and some crystalline; they fume slightly in air and readily absorb carbon dioxide. The piperazines form hydrates which are readily soluble in alcohol or chloroform but sparingly soluble in water. The poly-substituted pyrazines always give 2 isomeric piperazines on reduction. The lower piperazines have higher boiling points than the corresponding pyrazines whilst for the higher compounds this relation is reversed (Stöhr, J. pr. Chem., 1897, [ii.] 55, 49).

**PIPERIC ACID** v. RESINS.

**PIPERIDIN** v. RESINS.

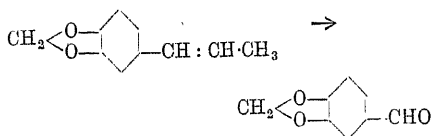
**PIPERIDINE** v. BONE OIL.

**PIPERIDINE GUIACOLATE** v. BONE OIL.

**PIPERINE** v. RESINS; also **VEGETO-ALKALOIDS**.

**PIPERONAL** (*Heliotropine*) methyleno-proto-catechic aldehyde,  $CH_2O_2 \cdot C_6H_2 \cdot CHO$ , was first obtained by Fittig and Miels (Annalen 1869, 152, 35) by the oxidation of piperinic acid and its constitution was established by Fittig and Remsen (*ibid.* 1871, 159, 158). It is closely

connected with various natural products including piperine, safrol and isosafrol, from all of which it may be obtained on oxidation. Piperonal itself occurs only to a limited extent in nature, being generally found in conjunction with vanillin and other aldehydes; it is found in small quantities in *Spicebush*, and also in certain vanilla fruits such as the vanillon or pompona (Göller, Chemist and Druggist, 1907, 65, 13). It has not been proved whether the characteristic smell of the flowers of the heliotrope variety, from which the commercial name is derived, is actually due to this compound. Piperonal, although not used in the preparation of scents and essences, is employed considerably for the purpose of soap perfumery and is now prepared in large quantities, especially by Schimmel and Co. The oxidation of isosafrol (Bericht von Schimmel & Co., April, 1893).



Otto and Verley have proposed to obtain piperonal by the action of ozone on safrol or isosafrol (D. R. P. 97620).

**Properties and reactions.**—White crystals, m.p. 37°, b.p. 263°, very slightly soluble in water, easily so in most organic solvents. With dilute hydrochloric acid, protocatechuic aldehyde is formed and carbon is said to be liberated. According to Schimmel (Chem. Zentr. 1910, i. 1829), the reaction is much more complicated; with phosphorus pentachloride there is formed piperonal chloride  $\text{CCl}_2\text{O}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ ; with sulphur chloride the reaction proceeds more smoothly; with water this compound yields protocatechuic aldehyde, so that the method of preparation from piperonal (Schimmel & Co., D. R. P. 165727); with sodium amalgam there is formed piperonyl alcohol and two isomeric hydro-piperoinis; aniline condenses to form piperonal anilide; ammonium sulphide forms dithiopiperonal; sodium sulphite forms an addition compound, as also does trinitrobenzene.

By condensation with  $\alpha$ -bromopropionic ester, piperonal may be converted into an acid which loses carbon dioxide, forming isosafrol (Wallach, Annalen, 1897, 357, 72).

**PISANGCERYLIC ACID**  $\text{C}_{22}\text{H}_{44}\text{COOH}$ , m.p. 71°, is obtained from Pisang wax.

**PISANG WAX** v. WAXES.

**PISOLITE** v. ARAGONITE.

**PISTACHIA LENTISCUS** v. SUMACH.

**PITCH.** Various substances met with in nature when submitted to distillation yield, in addition to fluid products, a residuum that on cooling assumes a more or less viscous or solid character; and, furthermore, at various places on the earth's surface extensive deposits are found consisting of black, resinous substances of similar appearance and properties. To these products have been assigned the terms of 'mineral pitch', 'asphaltum', and 'asphaltum'. Each of these substances possesses distinctive features, and each in its place fulfils important requirements in the arts.

**Bitumen, asphaltum, mineral pitch.** These

compounds consist of complex mixtures of hydrocarbons, and are found in many localities and under the most varied conditions. Probably the celebrated Pitch lake, situated in the island of Trinidad, and said to be upwards of three miles in circumference, represents one of the most important deposits of natural bitumen known, although within the past forty years many additional sources have been found in Cuba, Central and South America, California, Arkansas, Nicaragua, and Peru, in India, Palestine, Egypt, Turkey, Italy, France, Germany, Switzerland, Ho-Tsing, province of Szu-Tchuan, China, and Asiatic Russia.

The origin of these deposits is involved in considerable obscurity; they appear to have been formed by the oxidation of the unsaturated hydrocarbons in petroleum. Bitumen has been regarded either as a product of chemical action or as a distillate produced by natural causes from animal and vegetable remains. It has been argued that if the bitumen were the result of a purely chemical process, we should expect to find a generic uniformity in the character of the substance wherever found on the earth. On the other hand, if petroleum is the result of metamorphism, its generation is co-existent only with that of metamorphic actions. If we accept this hypothesis, the generation of petroleum must be considered as geologically recent.

In studying the asphalt of Bentheim, Patrono, Castro, Colla San Magna, and other places, the conclusions arrived at have confirmed the views of Mendeleeff to the effect that their formation has been brought about by inorganic means. Bitumen is frequently met with in places where, from a geological point of view, its occurrence can be explained only by assuming that it has accumulated within the fissures in the same manner as that contained in lavatic geodes, and separated from pre-historical tuffaceous deposits by inorganic means. Engler, who has given some considerable study to the Bentheim asphalt, furnishes the following particulars respecting it. It is insoluble in alcohol, ether, carbon disulphide, oil of turpentine, and similar solvents, but melts when strongly heated: sp.gr. 1.092. It contains:

	I.	II.
Carbon . . . . .	89.46	89.83
Hydrogen . . . . .	9.55	9.88
Ash . . . . .	1.09	1.14

Distillation yielded the following products:—

	I.	II.
Tar . . . . .	36.8	38
Coke . . . . .	48.9	48
Gas and water . . . . .	14.3	14

The tar obtained by the distillation of the asphalt on a large scale was free from phenol and creosotic compounds, and the products of its distillation were as follows:

	p.c.
Burning oils . . . . .	12.72
Gas and lubricating oils . . . . .	9.78
Paraffin . . . . .	1.50
Paraffin grease . . . . .	0.65
Coke from retorts . . . . .	46.09
Coke from tar . . . . .	0.86
Pitch . . . . .	1.52
Loss, gas and water . . . . .	26.88

100.00

Egyptian asphalt contains :

	p.c.
Carbon . . . . .	85.29
Hydrogen . . . . .	8.24
Oxygen . . . . .	6.22
Nitrogen . . . . .	0.25

The bitumen of Judea, found floating on the Dead Sea, contains :

	p.c.
Carbon . . . . .	77.84
Hydrogen . . . . .	8.93
Oxygen . . . . .	11.54
Nitrogen . . . . .	1.70

Sulphur is invariably present in natural bitumens, varying in quantity from 3 to 4.2 p.c. and even 10 p.c.; from such samples, hydrogen sulphide is always given off on heating. Asphalts and bitumens vary considerably in character. Generally, their appearance is that of smooth, hard, brittle, black, or brownish-black resin, breaking with a distinct conchoidal fracture: the sp.gr. varies from 1 to 1.7; when free from mineral matter they may be even lighter than water. When distilled with water, asphaltum yields a volatile oil called by Boussingault.

which remains when the petroleum is completely driven off, is a solid black substance resembling the original substance prior to distillation, but which does not soften below under about 300°, and decomposes below its fusing point.

Trinidad pitch yields, when heated—

	p.c.
Volatile organic matter . . . . .	76.75
Non-volatile organic matter . . . . .	17.77
Ash . . . . .	5.48

100.00

Natural bitumen is only partially soluble in alcohol, but more completely so in carbon disulphide, carbon tetrachloride, petroleum spirit, chloroform, oil of turpentine, coal-tar, benzene and naphthas; the pyridine bases, also derived from coal-tar, scarcely act upon it. The portion, however, that passes into solution communicates a strong greenish fluorescence to the liquid, and when . . . . . in the manner described . . . . . anthracenes for certain . . . . . 26, 190; 31, 35, 45), two distinct absorption bands are visible near the D line of the spectrum, from yellow to green, which distinguishes it from all other pitches, coal-tar excepted, which occasionally shows bands, but invariably situated in the blue portion of the spectrum near the F and G lines.

In petroleum spirit, 74.23 p.c. of its organic matter is soluble and 20.29 p.c. insoluble.

At a temperature varying from 58° to 60° bitumen softens, and it melts at about 100°, although varieties are met with that melt only at a much higher temperature.

The following table of results obtained by A. E. Jordan and given in Allen's Organic Analyses shows the difference between natural asphalts and artificial products.

Material.	Ash.	Organic matter.		Action of petroleum spirit.		
		Volatile.	Non-volatile.	Soluble.	Insoluble.	Percentage of organic matter soluble.
Asphalt (origin unknown) . . . . .	0.60	80.79	18.61	47.63	51.77	47.91
Trinidad pitch . . . . .	5.48	76.75	17.77	74.23	20.29	78.53
Petroleum pitch . . . . .	none	50.43	49.57	36.16	63.84	36.16
Shale oil pitch . . . . .	0.25	66.40	33.35	63.62	36.13	68.77
Coal-tar pitch . . . . .	0.15	49.33	50.52	18.56	81.29	18.58
Bone pitch (inferior) . . . . .	0.33	56.15	43.52	29.96	69.71	30.05

Boussingault's methods are not now used and the terms petroleum and asphaltum by him have received another meaning. That portion soluble in petroleum or acetone being known as petroleum and the portion insoluble in any of these liquids but dissolved by boiling turpentine or cold chloroform being known as asphaltene.

**Applications of asphaltum.**—The purer asphalts are employed almost exclusively for the manufacture of black varnishes and japans, for which purpose they are eminently adapted, yielding surfaces and coatings of great brilliancy and not prone to 'break up' or disintegrate. Asphaltum selected for the purpose of the varnish maker should be practically free from mineral matter or within a limit of 5 p.c., it should be completely soluble in carbon di-

sulphide, chloroform, high boiling coal-tar naphtha, and oil of turpentine (mineral matter excepted). It should break with a conchoidal fracture and brilliant lustre. It should not flow or lose shape, like wood tar and many of the fatty pitches, when left on a plane surface, and an angular fragment should retain its shape and the sharpness of its angles in boiling water.

**Asphalt rock.**—This is often met associated with . . . . . or the two variously admixed; in this condition the mineral is known as 'asphalt rock,' and occurs in the upper Jurassic formation interstratified with ordinary limestone.

The following figures, by Durant Clave, show the proximate composition of some rock asphalts employed for paving:—

	Val de Travers Switzerland.	Lobsann Alsace	Seyssel Ain France	Maestu Spain	Ragusa Sicily
Water and other matters volatilised at 100° C. . . . .	0.35	3.40	0.40	0.40	0.80
Bituminous matter . . . . .	8.70	11.90	9.10	8.80	8.85
Sulphur in organic combination or free state . . . . .	0.08	4.99	—	trace	—
Iron pyrites . . . . .	0.21	4.44	—	—	—
Alumina and oxide of iron . . . . .	0.30	1.25	0.05	4.35	0.90
Magnesia . . . . .	0.10	0.15	0.05	3.85	0.45
Lime . . . . .	49.50	38.90	50.50	5.70	49.00
Carbon dioxide . . . . .	40.16	31.92	39.80	8.15	39.40
Combined silica . . . . .	—	—	—	11.35	—
Sand . . . . .	0.60	3.05	0.10	57.40	0.06
	100.00	100.00	100.00	100.00	100.00

Native calcareous asphalt exhibits a brown or nearly black colour and breaks without evidence of cleavage. The fracture is earthy and granular, not unlike chocolate, both in appearance and colour. When long exposed to the air it loses this character and then resembles ordinary limestone: this change, however, only extends to the surface.

The specific gravity of rock asphalt is about 2.23. It is hard and may be broken with a hammer, but when warmed it may be softened to a kind of paste and at about 60° falls to powder.

Good rock asphalt is a hard, crystalline limestone. It is frequently veined, and contains large crystals of calcite impregnated with bitumen; this feature is considered an important indication, bad specimens or low qualities showing an absence of such impregnation, which renders them difficult to manipulate. Val de Travers, Seyssel, and other asphalt rocks, when powdered, give a fine, white powder with definite, but not sharp, edges, such as Trinidad pitch. The product of this mixture is technically known as 'mastic,' and in using it further additions of bitumen, shale oil, and grit are frequently made.

The following analysis by Durant Claye will convey a general idea of these compositions:

	Refined bitumen from Bastennes	Imitation asphalt made from coal-tar
Moisture . . . . .	0.30	0.60
Bituminous matters soluble in carbon disulphide . . . . .	69.35	20.65
Organic matter insoluble in carbon disulphide . . . . .	4.40	18.45
Alumina and oxide of iron . . . . .	2.85	2.65
Magnesium and calcium carbonates . . . . .	2.65	39.60
Silica . . . . .	20.35	18.05
	100.00	100.00

For determining the actual bituminous matter in asphaltic rocks, natural and otherwise, the air-dried sample is exhausted with suitable solvents, which may consist of carbon disulphide, Russian oil of turpentine or coal-tar benzene. The operation may be conducted in

a Soxhlet's tube, and if a correction be made for the moisture expelled at 100° the loss of weight furnished by the residue of bitumen removed.

The residue may be further checked by distilling off the solvent and weighing the residue, observing the usual precaution of drying at 100° until constant. The bitumen thus obtained should be heated further to 220°, when, if the sample is good, there will be little or no further loss of weight; if, however, volatile oils or petroleum be present, the loss may be considerable.

The volatile oil is best determined by repeatedly digesting the powdered sample with cold alcohol and weighing the residue; the exhaustion may be considered as complete when a portion of the alcoholic washing shows no turbidity on dilution with water.

If the residue left after exhaustion exhibits a dark colour, other organic constituents of valueless nature are present. Their proportion may be ascertained by igniting the weighed residue left after the removal of the bitumen, re-carbonating it with ammonium carbonate, again gently igniting it and re-weighing. The loss of weight represents the quantity of non-bituminous matter present.

Val de Travers asphalt gives up the whole of its organic matter to petroleum spirit, imparting a deep brown colour to the fluid, perfectly free from fluorescence, whereas the soluble portion of coal-tar pitch does not exceed 20 or 25 p.c., yielding a solution exhibiting a deep greenish fluorescence, a characteristic of this pitch in any of its solvents and which renders its detection alone or in admixture a matter of no great difficulty (*v. infra*).

#### Pitches derived from technical processes.

*Artificial pitches.* Coal-tar pitch may be looked upon as occupying the most prominent position in the series, both as regards the magnitude of its production and its corresponding purposes of artificial fuel, asphalts and varnishes.

Some idea of the extent to which this residue is produced in the United Kingdom, together with the industry springing out of it, may be gathered from the statement that according to the last census of production the total output of

tar for the United Kingdom was 846,000 tons, representing according to the same authority 647,000 tons of pitch, by far the larger proportion of which is consumed in the manufacture of patent fuel.

Coal-tar pitch is the residue remaining in the stills after separation of the various fractions known as naphthas, light oils, carbolic, creosote and anthracene oils, and amounts to about two-thirds of the weight of the tar operated upon. Its physical character is mainly dependent upon the temperature employed in distillation; but its ultimate chemical composition is more or less governed by the composition of the coal distilled. It may be either 'soft' or 'hard' or 'medium'; it may be either 'normal,' as a product resulting from the simple distillation of tar, or it may be otherwise, as when mixed with green or other tar oils before running from the stills. The selection of tar distillates to be used in thus thinning down a pitch carried to a full limit of distillation is important, as it has been found that when creosote or naphthalene is employed, a pitch is obtained lacking in binding or cementing power, and blocks or briquettes made from it are liable to crumble. This defect is only obviated by the use of the heavier distillates, such as green oils which are of a more viscid and adhesive character.

When pitch is passed through a red-hot tube it yields about 250 times its bulk of gases, chiefly hydrogen.

Pitch may be utilised by burning it into lamp-black, and, according to Thenius, 500 kilos. of pitch yield 200 kilos. of varying descriptions of lamp-black and 200 kilos. of coked residue.

Referring more generally to the several results that may be obtained by varying the fractions during the distillation of coal-tar, it may be stated that if the operation be terminated at the point at which the light oils only are driven off, the residue in the still, representing about 80 p.c. of the charge, may be used for the preparation of asphalts, under the name of 'refined' or 'prepared' tar, although it is very doubtful whether material of this character is to be met with in the present day. If about 10 p.c. more is run off, the residue is soft pitch; moderately hard and hard pitch

follow, the latter when the distillation is carried on as far as practicable in wrought-iron stills. The 'asphalt prepared' or 'refined tar' thus obtained by simply distilling off the naphthas and light oils, invariably contained all the constituents of the distillate that would follow if carried to its limit and collected apart, *i.e.* creosote oils, phenols, naphthalene, anthracene and higher boiling-point substances. Coal-tar pitch in its normal condition and as originally obtained, is a bright, black, lustrous substance, breaking with a well-marked conchoidal fracture; but as now met with it presents a more or less dull or greyish tint, due to the altered condition under which it is obtained. These are, firstly, distillation, in which steam, either superheated or otherwise, is injected into the still during the operation, and by which it can be pushed to a greater limit and more complete extraction of anthracene, without endangering the still; and, secondly, the admixture of the residual pitch with 'green' or other oils, in order to bring it to a consistency at which it may be run off with facility and yield a product that shall represent 'soft,' 'medium,' or 'hard' pitch at will.

The proximate composition of coal-tar pitch is by no means well understood. It invariably contains some of the higher boiling hydrocarbons of coal-tar, notably anthracene, phenanthrene, pyrene, chrysene, together with bitumen and free carbon. The ultimate percentage composition of coal-tar is given by Habets as:

	p.c.
Carbon . . . . .	75.32
Hydrogen . . . . .	8.10
Oxygen . . . . .	16.06
Ash . . . . .	0.43
	<hr/> 100.00

Small proportions of sulphur and nitrogen are also present, the former to the extent of 0.4-0.7 p.c. Treated successively with cold benzene, carbon disulphide, boiling benzene, and boiling alcohol, Habets obtained 23.54 p.c. of a black powder resembling anthracite and containing 91-92 p.c. of carbon, 3.1 p.c. of hydrogen, and 0.4-0.9 p.c. of ash.

Donath and Asriel (Chem. Zentr. 1903 i. 1099) give the following figures:—

—	C	H	N	S	Extract with			Residue
					Petroleum spirit	Benzene	CS <sub>2</sub>	
Soft pitch . . . . .	91.80	4.62	?	?	25.05	44.98	6.57	22.82
Medium pitch . . . . .	94.32	3.98	0.148	0.77	15.14	40.03	7.10	38.16
Hard pitch . . . . .	93.16	4.36	?	?	15.51	39.46	5.21	29.39

The extractions with benzene and carbon disulphide followed in rotation.

The specific gravity of hard pitch varies from 1.475 to 1.500. It is wholly insoluble in water but partially soluble in alcohol and more so in benzene or carbon disulphide. Cold petroleum spirit exerts but little solvent action upon it, but when heated it dissolves it to the extent of 18 to 23 p.c. The pyridine bases also dissolve the soluble organic matter from pitch,

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but somewhat tardily, and only with the assistance of heat.

Solutions of coal-tar pitch exhibit a deep yellow or brownish fluorescence, which is highly characteristic of this substance. When heated it exhales an odour equally characteristic and not easily mistaken for any other known pitch. The volatile organic matter given off ranges from 46 to 64 p.c.



A benzene solution of coal-tar pitch when examined spectroscopically shows a cutting out of the blue part of the spectrum, with occasional absorption bands between the F and G lines.

*Testing of pitch.* For the requirements of commerce, pitch has to be tested for its 'softening' and 'melting' point, and contract notes stipulate that a sample is to 'twist' fairly after immersion for two minutes in water at 60° but not under 50°, must contain at least 53 p.c. of 'volatile organic matter,' and must be free from any extraneous matter such as grit or sand.

The twisting and melting-point of pitch are ascertained by methods of comparative simplicity, only varying in trifling points and details. Probably the simplest and most readily followed is that of F. G. Holmes and is conducted in the following manner:

Several pieces of pitch are selected from different parts of the sample and cut to the size of half-inch cubes. These cubes are then supported on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 c.c. of water heated by any convenient means, at a uniform rate of 5° per minute, as indicated by a thermometer immersed in the water with the bulb about two inches from the bottom of the vessel.

The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises the pieces of pitch are removed from time to time and twisted or squeezed with the fingers and the temperature noted at which they assume the following conditions:

(1) Readily twisting or soft, *i.e.* when the pitch can be easily twisted round several times.

(2) Very soft, *i.e.* when it yields to a very light pressure of the finger.

(3) Fused, *i.e.* when the pitch melts off the wire.

Soft pitch softens at 40° and melts at about 60°.

Moderately hard pitch softens at 60° and melts at about 80°.

Hard pitch softens at 80° and melts at about 120°.

The estimation of the volatile matter is conducted in the same way as in the case of coal and other bituminous substances, *viz.* by heating about 1 gram of the pitch to be examined in a platinum crucible of 1½ to 1¾ inches height with the cover on, which should have a small aperture in the centre. The heat is applied by means of a good Bunsen burner, first gently until no more smoke and vapour issue from the opening in the lid, finally as strongly as the burner will permit. The operation may last 20 minutes. The crucible is then placed in a desiccator and, after cooling, the residual coke is weighed; it ranges from 36 to 53 p.c. Fixed carbon and coke dust may be determined by successively exhausting with benzene, carbon disulphide, and alcohol, employing a Soxhlet tube for the extraction.

Methods for testing the softening point of pitch have been described by Muck (Z. f. Berg. Hutten u. Salinenwesen, 1889); Schewk zu Schweinsberg (Zeitsch. angew. Chem. 1890,

704); Mabery and Sieplein (J. Amer. Chem. Soc. 1901, 20, 16); Kraemer and Sarnow (Chem. Ind. 1903, 55).

The suitability of a pitch for the purpose of artificial fuel may be ascertained by carefully distilling a given quantity of the sample in a glass retort and noting the character of the distillates; when creosote or naphthalene have been used in thinning or diluting before running from the still they are accompanied with a considerable sublimate of naphthalene passing over at a comparatively low temperature; green oils do not yield naphthalene in this manner or sublimes that may be mistaken for it.

J. E. Mills (Bulletin 343, U. S. Geological Survey), gives the following tests employed at the U. S. Government fuel testing works, St. Louis, for the testing of briquette pitch.

1. The material is distilled; all coming over below 270° is rejected as valueless. 2. The flowing point is determined by placing about 3 c.c. of pitch in the bottom of a test tube ¾-inch in diameter and inserting it in a bath. The temperature of the bath is raised until, on taking out the tube and inverting it, the pitch flows 1 inch down the tube in 15 seconds. This point should be not less than 70°. 3. The pitch is extracted with CS<sub>2</sub>. The smaller the amount of residual carbon the more satisfactory the pitch. The higher the flowing point the better the briquettes stand in the fire.

*Applications and uses of coal-tar pitch.* Coal-tar pitch is extensively used in the manufacture of patent or artificial fuel, varnishes, japans, and asphalts, the trade in the first-named product having assumed enormous proportions. Fuel of this description consists of admixtures of coal-tar pitch with small coal or slack, compressed into the form of blocks and known under the name of 'briquettes.' This industry would seem to be due to Ferrand and Marsais who, in 1832, obtained a French patent for using coal-tar for this purpose.

Marsais, since 1842, employed soft pitch, and in that year commenced the works at Berardy, near Saint Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The manufactured fuel was sold in that country under the name of 'peras.' The manufacture of patent fuel has opened up wide channels for the consumption not only of the immense quantities of 'slack' obtained wherever mining operations for coal are carried on, but for the almost equally large bulk of pitch resulting from the operations of the tar distiller.

This industry has developed considerably as the following figures for the output in the year 1909, taken from the Government reports, show:—

#### *Production of Briquettes in 1909.*

Austro Hungary	117,599 metric tons
Belgium	2,707,390 "
France	3,061,300 "
Germany (Brown coal included)	18,748,713 "
United States	126,700 "
United Kingdom	1,511,645 Eng. tons

In the manufacture of briquettes, certain conditions are observed, regulating shape,

dimensions, and weight. The form should be that of a parallelepipedon, and they should not weigh more than 22 lbs.; they should possess a firmness approaching that of natural coal, and to attain this end the proportions of pitch used in their fabrication must be at least 5-7 p.c. They should not yield more than from 6.5 to 6.75 p.c. of ash, if intended for locomotive use, or 10 p.c. if for steamboat use.

When broken they should fracture with a clean, bright, and granular surface in the absence of which they are generally faulty. Their regular shape permits of facilities of stowage, and the loss in transit by disintegration does not amount to more than 1 or 2 p.c. against 30-50 p.c. as with coals. They should not fall to pieces in the fire but agglomerate into a firm compact coke.

Patent fuel of good quality is said to yield 10 p.c. more heating power than steam coal; it makes less dirt and when manufactured from hard pitch gives less black smoke than most kinds of coal.

In the preparation of artificial fuel of this character numerous attempts have been made to employ fatty, oily, mucilaginous, and similar substances or coal-tar, as the agglomerating or cementing medium, but the only materials now used are soft or hard pitch derived from coal-tar.

The operation of blending is comparatively simple, requiring little plant beyond that of melting pans or pug mills. Occasionally, when hard pitch is employed, a mixture of this material with coal, both in fine powder, is subjected to the action of superheated steam, by which the compound is softened and yields a compact conglomerate on cooling.

In shaping or forming such mixtures of coal and pitch into blocks or briquettes, presses with open and closed moulds are in use. The process scarcely requires description, being quite analogous to that of moulding bricks, the machine that works with dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies).

*Black varnishes and japans.* In the preparation of varnishes, japans, and paints for coating and protecting the surfaces of iron and wood, tar pitch is simply dissolved in, or melted with, a suitable coal-tar distillate, depending on the purpose to which the product is to be applied and the rate at which it is required to dry or become hard. These solvents vary from the more volatile benzene to the heavier xylenes or solvent naphthas, and it is not an unusual thing to employ naphthas and light oils as run from the still, up to actual cresote. No special knowledge or plant is requisite in compounding them beyond that well known to varnish makers.

As a rule the pitch should be melted at the lowest temperature, and the solvent in the first instance added in small quantities, after which it may be introduced more freely up to the desired consistency. Rosin, in varying proportions, is occasionally added, but in the majority of cases pitch alone is used. Varnishes, so prepared, will obviously vary in character, drying quality, and lustre, and it is hardly necessary to point out that when required of a nature that shall dry rapidly and with a bright

uniform surface both the pitch and the solvent employed should be free from water.

Tar varnishes dry with a bright, hard surface, and adhere both to wood and iron with considerable tenacity. They have been extensively employed for coating the hulls of iron ships as anti-fouling compositions and for the purposes of protective paints generally.

*Asphalts and compounds for paving.* Asphalt prepared from substances derived from coal-tar has found a wide application, especially for the purpose of street paving; surfaces of ground coated or covered with asphalt become impenetrable to moisture and the passage of noxious effluvia. Coal-tar asphalt may be regarded as a soft pitch to which body or firmness has been imparted by incorporating sand, grit, gravel, chalk, lime, and substances of a similar character. The soft pitch used for this purpose may consist of the residue from tar after distilling off the more volatile constituents, and known as refined or prepared tar; or it may consist of hard pitch, afterwards melted and thinned down to the required consistency with heavy tars or green oils.

The use of this pitch into asphalt suitable for street paving is carried on in various ways. Occasionally the pitch is melted in iron pans and the ingredients to be incorporated simply added and well stirred in the mixture which contains 20-30 p.c. of pitch, and is used while hot and in a plastic condition.

Asphalt, in the form of blocks or slabs, is manufactured for similar purposes, melted pitch being run direct into a pug mill in which it is incorporated with the proper proportion of sand, gravel, or grit, and from this mill the mixture is run direct into sand moulds to harden and solidify.

Tar asphalt is said to be considerably improved by the addition of about 5 p.c. of sulphur, added in small portions at a time during the heating or making. Much hydrogen is given off, and during the heating the sulphur constituents rich in hydrogen the residue less fusible. Starting with soft pitch or viscid tar, it is said that 75 p.c. may be obtained as a good asphalt, which does not soften in boiling water.

*Coal-tar asphalt,* or more correctly, very soft pitch, is also employed for constructing 'asphalt pipes.' This industry was introduced by Jaloreau and has been fully described by Behrens (Dingl. poly. J. 208, 377). Endless hemp paper, 7 feet wide, is passed through a semi-cylindrical pan set in a furnace and filled with hot pitch. A roller revolving in the pan takes up the paper saturated with pitch and conveys it to a similar roller forming the core of the pipe, round which any number of layers of paper may be wound. When the desired thickness has been attained, fine sand is dusted on and the cylinder is exposed to considerable pressure. After cooling in water the core is withdrawn and the pipe becomes ready for use. Pipes manufactured in this manner resist very considerable pressure from within. They possess many features of value for special uses and are employed for conveying water, acids, air-blasts for pit ventilation, and for conveying underground telegraph wires.

A tarred paper is manufactured for packing. Another description which has been used for papering damp walls consists of two layers of paper united by a coating of pitch.

A further and more important application of materials, such as paper and felts, saturated with 'prepared or refined tar,' or pitch let down to the required consistency by solution in heavy tar oils, is for the purpose of 'roofing paper or felt.' A considerable quantity of this material is manufactured in Germany and elsewhere.

Owing to the introduction of motor vehicles, the question of reducing the nuisance caused by dust on the roads has become very important and much attention has been given to it. It has been found that roads pitched or prepared tar as a binder not only are less dusty but are more durable and cost less for repairs, maintenance and cleansing. Several patented articles for use as road binding agents have been put on the market, most of which consist essentially of soft pitch. This outlet has an important bearing on the pitch industry, as if a large proportion of the tar produced in the country is used for road making the output of pitch available for briquetting and other purposes will be very materially reduced.

#### Pitches derived from the distillation of fatty substances.

'Stearine' and 'palm pitches.' Several pitches of this character are met with in commerce, notably those known as 'stearine' or 'cotton oil,' 'wool oil,' and 'palm pitch'; the two first-named representing residues from substances consisting mainly of stearic, the third of palmitic acid. Their manner of preparation is as follows:

In the purification of crude cotton seed oil by caustic soda, a more or less viscid residue is obtained, known as 'foots' or 'mucilage,' which consists largely of stearic acid in the form of an imperfectly formed soap. This material constitutes an article well known in Hull, Liverpool, London, and other centres of cotton oil refining, which has been extensively dealt with for the recovery of its 'stearine' and pitch. The soapy mucilage thus obtained in the first instance is heated in suitable vessels, and then gradually decomposed by the addition of dilute sulphuric acid. This treatment separates the 'fatty acids' or 'stearine' in the form of a perfectly black greasy substance, technically known as 'black grease,' which may vary in quantity from a few p.c. to 80 p.c.

The recovery of 'stearine' and stearine pitch follows as a second step in the operation, and consists in submitting the 'black grease' so obtained to a process of distillation by the aid of superheated steam, giving the following yield:—

Inferior oils	6 p.c.
'Stearine'	39 "
Pitch	50 "
Loss	5 "

100

The pitch thus obtained and constituting the larger portion of the operation, may be 'hard' or 'soft,' varying with the point to which the distillation has been carried. Both are produced and met with in commerce as meeting the requirements of their respective consumers and present the following characters:

Soft stearine pitch, a viscid treacly substance, and hard stearine pitch, a firm, bright, black product, breaking with a well-marked conchoidal fracture. The sp.gr. of this pitch is about 1.35. At 55° it softens sufficiently to twist in the manner referred to under coal-tar pitch, and at 95° to 100° it melts. It is almost completely soluble in benzene and the pyridine bases, but to a much lesser degree in petroleum spirit. To this solvent stearine pitch only gives up about 71 p.c. of its organic matter, 23 p.c. remaining insoluble. Sulphur is present to the extent of 0.04 to 0.06 p.c.

It yields 79 p.c. of volatile organic matter and 21 p.c. of coke, containing 5-6 p.c. of mineral matter or ash. During the operation of heating and burning off a strong, fatty odour is evolved which at once indicates its origin and nature as an oil pitch.

A benzene solution exhibits no bloom or fluorescence, and when examined spectroscopically a cutting out of the blue or violet portions of the spectrum only; no absorption bands are visible. Stearine pitch has been extensively used for the preparation of special black varnishes used in painting tarpaulins and in various compounds employed for electrical insulation. For these purposes it is eminently adapted from its resistance to surfaces and combinations both supple and pliant, and that do not crack and disintegrate in the manner of some mineral pitches.

*Wool-oil pitch.* In the scouring and washing of woollen goods, soapy liquors are obtained in considerable quantity. These liquors are now treated for the fatty substances contained in them. The process followed is in many ways analogous to that already described, the fatty acids being separated by heating and addition of dilute sulphuric acid. On submitting these fatty acids to a similar process of distillation, an excellent stearine is recovered with a similar residue of pitch. This pitch may be hard or soft, and in both stages resembles that known as cotton or stearine pitch; it has similar uses.

The softer kinds are used as lubricants in heavy machinery under the name of 'hot and cold neck grease.'

*Palm oil pitch.* This pitch, which is now produced in considerable quantity, is the residue of an operation extensively carried out more or less in accordance with an important patent granted to Wilson and Clayton in the year 1843, in which oils or other fatty substances were heated with sulphuric acid in place of an alkali for separation of their contained fatty acids.

In the operation claimed, the glycerol is converted into 'sulphoglyceric acid,' which is afterwards washed out, and the resultant black mass distilled with superheated steam. The respective fatty acids pass over in a condition of great purity and suitability for the various purposes applied. With palm oil, palmitic acid distils over, and palm pitch remains in the still.

In appearance and when soft, this pitch varies from those already described. It is dull in colour, with a waxy feel, but when hard is tolerably bright and black in colour, breaking with a distinct conchoidal fracture and small granular surface, but exhibiting the same waxy feel: its sp.gr. varies from 1.045 to 1.050. The softer kind twists at the ordinary temperature; the harder at 30°, although it does not completely melt under 95°. It yields about 80 p.c. of volatile organic matter and 20 p.c. of a light porous coke, containing 0.5 to 0.8 p.c. of ash. During heating a powerful fatty odour is given off, betraying its nature as being also of fatty origin. It is almost wholly soluble in benzene, but scarcely acted upon by the pyridine bases or petroleum spirit. A solution examined spectroscopically shows a cutting out of the violet portions of the spectrum but no absorption bands.

Palm pitch has been extensively used for tarpaulin varnishes, and in combination with paraffin wax, for various electrical insulators. The softer kinds are employed as hot and cold neek greases for heavy machinery.

*Bone oil pitch.* In the dry distillation of bones and other animal substances, an oil is obtained exhibiting a strong fœtid odour and known as bone or 'Dippel's oil' (*oleum animale Dippelii*) (q.v.), which when submitted to further distillation yields about 23 p.c. of a hard, firm pitch.

Hard and soft varieties are produced and present the following characteristics: jet black and shining; brittle, and breaking in masses, although distinctly conchoidal; sp.gr. ranges from 1.125 to 1.130. The harder pitches 'twist' at a temperature of 70°, and melt at 98°-100°.

A good sample will yield 63 p.c. of volatile organic matter and 37 p.c. of hard, compact coke, containing from 0.4 to 0.7 p.c. of mineral matter or ash. During the operation of heating and softening, the characteristic and unmistakable odour of bone or animal oil becomes very powerful and readily distinguishes it from all other pitches. As a solvent, benzene attacks it very imperfectly, but the pyridine bases dissolve it entirely or with the exception of a small quantity of carbonaceous matter. Petroleum spirit dissolves about 30 p.c. Solutions of this pitch in the pyridine bases exhibit no bloom or fluorescence, and when examined spectroscopically merely a cutting out of the violet portion of the spectrum, no absorption bands being visible. Sulphur is present to the extent of 0.30 p.c.

It exhales a somewhat unpleasant odour, very noticeable when warmed. Its chief uses are for tarpaulin and other varnishes.

*Stockholm pitch (wood-tar pitch).* Wood-tar, when submitted to distillation, yields distillates of light oils varying in sp.gr. from 0.840 to 0.880 and about 70 p.c. of pitch. In appearance it is jet black and brilliant, but it is inferior to bone pitch. Its fracture is conchoidal, but it is extremely brittle, crumbling between the fingers. It is slightly adhesive and becomes sticky on gently warming. It has a sp.gr. of about 1.105; at 40° it twists easily and at 82° it melts. When heated and ignited it yields 88-88.5 p.c. of volatile matter, leaving a soft,

friable coke ranging from 12-11.5 p.c. and containing from 0.7-0.84 p.c. mineral matter or ash. During the burning off, vapours and odours are evolved impossible to mistake for those of any other pitch, or for other than that of wood tar. Benzene dissolves this pitch completely and the pyridine bases equally well; but petroleum spirit only takes up from 91 to 92 p.c., leaving a small portion insoluble. Sulphur is present but in minute quantity only, not exceeding 0.01 p.c.

A solution of Stockholm pitch shows no bloom or fluorescence, and when examined spectroscopically a cutting out of the violet spectrum only. No bands are visible nor any indication of chrysene, said to exist in this particular tar or pitch.

Stockholm pitch dissolves almost completely in alcohol and potash lye. When its alkaline solution is boiled a coloured oil passes over possessing a stupefying smell, and when acidified and boiled yields volatile fatty acids. A black mass is deposited as the operation proceeds; on boiling this mass with water, creosote is given off. If the acid and alkaline treatment is repeated several times, the mass is converted into a black powder which, after long boiling with hydrochloric acid, yields to alcohol only a small quantity of resin. The black residue insoluble in alcohol and potash consists of—

	p.c.
Carbon . . . .	65.04
Hydrogen . . . .	4.89
Oxygen . . . .	30.07
	100.00

As wood-tar is a complex mixture of phenoloid bodies, amongst which guaiacol and cresol predominate, and the less volatile fractions contain methyl ethers of pyrogallol and its homologues, it is highly probable that the residual pitch resulting from its distillation at a comparatively low temperature contains amongst its other constituents the methyl ethers of trihydric phenols (v. CREOSOTE).

Wood-tar pitch is assumed to possess much of the antiseptic and preservative power of the tar from which it is derived. It finds a considerable outlet for marine purposes and the coating and painting of ships.

*Rosin pitch.* Rosin or colophony, is the residue left on distilling off the volatile oils from crude turpentine, and when submitted to further distillation, yields definite products, but varying with the temperature and conditions. In a vacuum or current of superheated steam it may be distilled almost unaltered, but when subjected to dry distillation, as in the ordinary method pursued by rosin distillers, it yields a number of products, consisting chiefly of rosin oil, which passes over to the extent of about 85 p.c., including rosin spirit, water, a powerfully anæsthetic gas containing carbon monoxide, ethylene, butylene, pentene, with a residue of pitch amounting to 1½ cwt. from a ton of rosin.

Rosin pitch is a yellowish-brown substance, hard and compact but easily crumbling on slight pressure. It has a sticky feel, and when warmed exhibits the characteristic odour of rosin. Its sp.gr. varies from 1.090 to 1.095;

at a temperature of 35° it twists readily, and at 68° melts. When heated and ignited it yields 82.5 p.c. of volatile matter, leaving a spongy soft coke amounting to 17.5 p.c., which contains 0.58 to 0.7 p.c. of mineral matter or ash. During the heating a strong odour of rosin is given off, readily distinguishing it from Stockholm or wood-tar pitch. In benzene and the pyridine bases it is completely soluble, but petroleum spirit only takes up 86.94 p.c., leaving 13.06 p.c. insoluble: sulphur is present to the extent of 0.26-0.3 p.c.

Solutions of rosin pitch exhibit a deep greenish bloom or fluorescence, but differing from that of coal-tar pitch, which is invariably yellow. Spectroscopically, they merely show a cutting out of the blue and violet portions of the spectrum; absorption bands are absent.

Rosin pitch finds no special use by itself, but is occasionally mixed with other pitches of an inferior description.

*Pitches derived from the distillation of petroleum and allied substances.* Of these products, ozokerite pitch occupies the most important position. It is obtained from the distillation of crude ozokerite, and the following figures have been furnished by E. J. Mills as representative of the operation:—

Very light oils . . . . .	20
Heavy oils . . . . .	50
Paraffin . . . . .	8
Hard pitch . . . . .	8
Loss . . . . .	14
	100

B. Redwood (J. Soc. Arts, 34, 886) gives the products of Galician ozokerite as 5 p.c. of gaseous hydrocarbons, 3 p.c. of naphtha, 6 p.c. of semi-paraffin, 12 p.c. of soft paraffin (melting at 44°-46°), distilled ozokerite (melting at 61°), and black waxy residue. It is a hard, waxy substance breaking with a rough granular surface, and irregular fracture. Its colour is dark amber, inclining to brown; its sp.gr. is 0.950. At a temperature of 50°, it twists and at 85° melts; heated and ignited it yields 9.7 p.c. of volatile organic matter, leaving 3 p.c. of soft, friable coke containing traces only of mineral matter or ash. During this operation the odour evolved is simply that of highly-heated paraffin. It is completely soluble in benzene but not wholly so in the pyridine bases, the solution showing no bloom or fluorescence. Examined spectroscopically, no absorption bands are shown, but a cutting out of the blue and violet portions of the spectrum only, as is the case of the rosin pitch described.

Ozokerite pitch have been found to possess remarkable electrical qualities, and in admixture with various substances, caoutchouc among them, have formed the subject matter of several patents. Such compounds have found extensive uses for coating telegraph wires and for insulating purposes generally.

*Petroleum pitch.* In the first distillation of crude petroleum oil, the charges may be run down to a coking point or they may be discontinued at a stage at which pitch or artificial asphaltum would result on cooling.

In appearance it greatly resembles natural

bitumen or asphaltum; it is jet black and shining, and breaks with a similar conchoidal fracture. It has a sp.gr. of about 1.120. At a temperature of 45° it 'twists,' at 84°-85° melts; heated and finally ignited it yields about half its weight of volatile organic matter. The odour evolved is characteristic of petroleum, but differs entirely from that of natural asphaltums, with which it cannot be confounded. Mineral matter is present in minute traces only. Benzene dissolves this pitch completely, affording a solution exhibiting a strong yellow bloom or fluorescence not unlike that observed with coal-tar pitch. It is, however, almost insoluble in the pyridine bases; petroleum spirit dissolves 36.16 p.c. only. The residues from American petroleum contain notable quantities of closed chain hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogen, and pyrene have been recognised, as also a hydrocarbon called thallene. From Californian petroleum the hydrocarbon piceene  $C_{22}H_{14}$  has been isolated. When treated with sulphuric acid, it yields a sulphonic acid dissolving in water with a splendid blue green fluorescence. Petroleum pitch, although differing in its physical aspect, may, in many respects, be looked upon as resembling coal-tar pitch.

B. Poro (Gazz. chim. ital. 13, 77) gives the following figures as showing the results of the distillation of petroleum:—

	I.	II.
Oil . . . . .	63.5	66.9
Pitch . . . . .	32.2	28.3

Petroleum pitch has been used in compounding cements, asphalts, varnishes, and patent fuels.

*Shale oil pitch* is now quite unknown, manufacturers of shale oil preferring to continue its distillation to the extent of coking.

*Bibliography.*—Lunge's Coal Tar and Ammonia (4th edit.), 1909; Allen, Commercial Organic Analysis (2nd edit.), 1886; E. J. Mills, Destructive Distillation; S. F. Peckham (Amer. J. Sci. [iii.] 28, 105-117); Striiplemann and Engler (Dingl. poly. J. 250, 216, 227, 271, 316, 321); Boussingault (Compt. rend. 96, 1452, 1456); B. Dolachanal (*ibid.* 97, 491, 494); S. Bernus (Bull. Soc. chim. de Belgique, 1911, 7).

**PITCHBLENDÉ, or Uraninite** (Ger. *Uranpecherz*). A uranium mineral which is much sought for as an ore of radium. Its occurrence in the ancient silver mines at Joachimsthal in Bohemia was known as early as 1727; and it was in this mineral that M. H. Klaproth discovered in 1789 the element uranium. The old German names Pecherz, Pechblende, &c., were suggested to the miners by a superficial resemblance of the mineral to pitch and to zinc-blende. The name Uranin, proposed by W. Haidinger in 1845 and later modified by Dana into Uraninite, is sometimes used in a rather wider sense to include the massive variety (pitchblende) and the crystallised varieties ('uranoniobite,' cleveite, bröggerite, and nivenite).

The mineral, although possessing certain points of considerable interest and a high value, is unattractive in appearance. It is opaque and black with a dull pitchy lustre (crystals are

brighter and with a sub-metallic lustre) and breaks with a sub-conchoidal to uneven fracture. The streak, or colour of the powder, is brownish- or greenish-black. The only feature that attracts attention is the remarkably high density (sp.gr. 6.4-9.7). This feature serves to distinguish the mineral from the more commonly occurring chromite; in its non-magnetic character it differs from magnetite; and in the absence of cleavage from wolframite—these being minerals often mistaken by prospectors for pitchblende. From some other heavy black minerals, such as columbite and tantalite, the distinction is less easy in the absence of chemical tests. Pitchblende can, however, always be quickly and readily recognised by means of its radio-active character; and without the aid of such simple and portable instruments as the spinthariscopes (or scintilloscopes) and gold-leaf electroscope the chances of the prospector are small. Although actively sought for since the discovery of radium in 1898, it is a remarkable fact that no new deposits of pitchblende of any importance have been brought to light.

Two distinct varieties, with very different modes of occurrence, are known. One is met with in a massive form, sometimes showing a mamillated or botryoidal surface, in mineral veins together with ores of silver, lead, copper or tin, and frequently associated with ores of nickel, cobalt, and bismuth. The other variety is found as small (1-3 cm. across) octahedral or cubo-octahedral crystals in veins traversing granitic rocks. These two varieties differ somewhat in chemical composition and in sp.gr. (6.4-8 for the massive, and 7.5-9.7 for the crystallised variety).

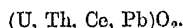
The mineral has been variously regarded as an oxide of uranium or as a uranate of uranyl, lead, thorium, &c. In composition it is subject to wide variations. The principal constituents are uranous and uranic oxides, but these are present in varying relative proportions. Lead is also invariably present, but it is only the crystallised varieties that contain in addition thorium and metals of the cerium and yttrium groups. Some of the many constituents shown in the analysis are no doubt present as mechanically admixed impurities, this applying more particularly to the massive variety of lower specific gravity. Thus an analysis by F. Janda (Oesterr. Zeitsch. Berg- u. Huttenw., 1902, i. 283; abstr. Chem. Zentr. 1902, ii. 150) of an average sample of the Joachimsthal ore gave:  $U_3O_8$ , 49.95;  $As_2S_3$ , 0.71;  $PbS$ , 1.85;  $PbO$ , 0.25;  $Cu_2S$ , 1.12;  $Bi_2S_3$ , 0.31;  $Ag_2S$ , 0.04;  $FeS$ , 7.93;  $Fe_2O_3$ , 1.14;  $FeCO_3$ , 6.96;  $Al_2O_3$ , 3.25;  $ZnO$ , 1.09;  $MnO$ , 0.11;  $CaCO_3$ , 3.69;  $CaSO_4$ , 0.89;  $MgCO_3$ , 0.76;  $MgSO_4$ , 0.07;  $SiO_2$ , 18.55;  $V_2O_5$ , 0.02;  $H_2O$ ,  $Na_2O$ ,  $K_2O$ ,  $P_2O_5$ , 1.34;  $PbSO_4$ ,  $CuSO_4$ ,  $Ni$ ,  $Mo$ ,  $W$ ,  $Ra$ , traces.

Several (22) detailed analyses have been made by W. F. Hillebrand, but he failed to arrive at a definite formula for the mineral (Amer. J. Sci. 1890, 40, 380; Bull. U.S. Geol. Survey, 1891, No. 78; 1892, No. 90; 1910, No. 419). The following analyses, I-V, are by Hillebrand. I, bright crystals from Branchville, Connecticut. II, massive from Johanngeorgenstadt, Saxony; III, massive from Gilpin Co., Colorado; IV, crystals ('brüggerite')

from Änneröd, Norway; V, crystals ('cleveite') from Arendal, Norway; VI, (W. Marckwald, Centr. Min. 1906, 761), crystals from Lukwengule, Uluguru mountains, German East Africa.

	I.	II. <sup>1</sup>	III. <sup>2</sup>	IV.	V.	VI.
$UO_2$	72.25	59.30	58.51	46.13	24.18	87.8
$UO_3$	13.27	22.33	25.26	30.63	41.71	—
$ZrO_2$ }	7.20	nil	7.59	0.06	—	—
$ThO_2$ }	—	nil	—	6.00	—	—
$CeO_2$	—	nil	0.22	0.18	—	—
$(La,Di)_2O_3$	—	nil	—	—	—	—
$(Y,Er)_2O_3$	—	nil	—	1.11	9.76	—
$PbO$	4.35	6.39	0.70	9.04	10.54	7.5
$FeO$	—	—	0.32	—	—	1.0
$Fe_2O_3$	0.11	0.21	—	0.25	0.03	—
$MnO$	0.10	0.09	0.16	—	—	—
$CaO$	0.18	1.00	0.84	0.37	1.06	2.1
$MgO$	—	0.17	tr.?	tr.	0.10	—
Alkalis	—	0.31	tr.?	tr.	0.23	—
$H_2O$	0.68	3.17	1.96	0.74	1.23	0.5
He, &c.	n.d.	tr.	0.02	0.17	n.d.	—
$SiO_2$	0.03	0.50	2.79	0.22	0.90	0.3
$P_2O_5$	—	0.06	0.22	0.02	—	—
Insol.	0.04	—	—	4.42	1.10	0.2
	98.21	97.93	99.82	99.61	94.50	99.4
Sp.gr.	9.733	6.89	8.068	8.893	7.50	8.84

In signs of alteration there is more uranic oxide ( $UO_3$ ) and water. The latter pass into the alteration-product known as gummite, which contains only uranic oxide together with much water. Since the dioxides of uranium, thorium, and cerium have been obtained artificially as cubic crystals, it seems probable that uraninite may be regarded as an isomorphous mixture of these oxides, the formula then being



This view is supported by the discovery of the closely allied cubic mineral thorianite (*q.v.*), in which thorium oxide predominates over uranium oxide.

Containing a higher percentage of uranium than any other mineral, pitchblende is correspondingly richer in radium, but this amounts to only one part in five million (*i.e.* about 200 mg. per ton). About 0.1 gram of radium chloride can be extracted from a ton of ore containing 50 p.c.  $U_3O_8$ . On the process of extraction employed at the Joachimsthal works, see L. Haitinger and K. Ulrich, Sitz.-ber. Akad. Wiss. Wien, 1908, 117, [iia] 619. The inert gas liberated from pitchblende when the mineral is dissolved in acid or when heated *in vacuo* was first detected by W. F. Hillebrand in 1890, and believed by him to be nitrogen. This led Sir W. Ramsay in 1895 to the discovery in this mineral of terrestrial helium. Argon is also present.

By its alteration in nature pitchblende gives rise to a number of secondary uranium minerals. These are yellow in colour, and are often to be seen as an earthy coating on the surface of pitchblende: when met with oxidised zones of mineral-veins,

<sup>1</sup> Anal. II. includes also:  $Al_2O_3$ , 0.20;  $P_2O_5$ , 0.75;  $CuO$ , 0.17;  $As_2O_5$ , 2.34;  $V_2O_5$ ,  $MoO_3$ ,  $WO_3$ , 0.75;  $SO_3$ , 0.19.

<sup>2</sup> Anal. III. includes also:  $As_2O_5$ , 0.43;  $CuFeS_2$ , 0.12;  $FeS_2$ , 0.24;  $ZnO$ , 0.44;  $TiO_2$ , trace.

they form a valuable indication of the presence of the mineral. By simple oxidation and hydration it passes into gummite—a heavy, reddish-yellow mineral with a gummy appearance. In the presence of sulphuric and carbonic acids (the former produced by the oxidation of iron-pyrites commonly of pitchblende), it alters to a number of hydrated and basic uranium sulphates and carbonates—the so-called uranium-ochres (johannite, liebigite, &c.). In the presence of phosphatic solutions it gives the so-called uranium-micas (autunite, *q.v.*, torbenite, &c.).

The localities at which pitchblende has been found are relatively few in number, and it is only in three districts that the mineral has been found in quantities sufficient for mining. These are in the mineral-veins of Cornwall, of the Erzgebirge on the borders of Saxony and Bohemia, and in Gilpin Co., Colorado.

In Cornwall, the workable deposits are those of the South Terras mine in the parish of St. Stephen-in-Brannel near Grampound Road, and the Trenwith mine at St. Ives. The occurrence of pitchblende has, however, been recorded in some 25 other Cornish mines in the parishes of St. Just-in-Penwith, St. Ives, Penzance, Gwinear, Camborne, Illogan, Redruth, Gwennap, Wendron, St. Gluvias, Perranarworthal, St. Stephen-in-Brannel, and Lanivet. On the Saxon side of the Erzgebirge it has been found at Johanngeorgenstadt, Schwarzenberg, and Gottesberg; and on the Bohemian side at Joachimsthal and Schlaggenwald. (On the mode of occurrence at Joachimsthal, see J. Stöp and F. Becke, *Sitz.-ber. Akad. Wiss. Wien*, 1904, 113, [i.] 585.) Other European occurrences are in the mineral-veins of Příbram in central Bohemia, and Rezbanya in Hungary. A specimen has also been described from near Adrianople in Turkey (J. L. Smith, 1848). Near Central City in Gilpin Co., Colorado, pitchblende is worked on the Wood and Kirk lodes. A specimen of doubtful origin has been described from New South Wales (T. H. Laby, 1909). The localities above mentioned all refer to the occurrence of massive pitchblende in mineral-veins.

The crystallised varieties occur as small crystals sparsely scattered in pegmatite-veins, and are occasionally met with as isolated specimens in the felspar quarries in the south of Norway, at several places in the neighbourhood of Moss (Karlshus, Raade, Ånnerød, Elvestad, Huggenåskilen, Skraatorp), near Arendal (Garta quarry and Tvedestrand), and in Sørsdalen (Eyje). In the United States, crystals have been found in the felspar quarries at Middletown, Glastonbury, and Branchville in Connecticut. In the Flat Rock mine and other mica mines in Mitchell Co., and Yancey Co., in North Carolina. At Marietta in South Carolina; Barringer Hill in Llano Co., Texas; and rather abundantly in the Bald mountain district in the Black Hills of South Dakota. A Canadian occurrence is in mica mines at Villeneuve, Ottawa Co., Quebec. Finally, crystals have recently been found in a mica mine at Lukwengule in the Uluguru mountains, German East Africa.

Curiously, this ore, now of such great value,

was a source of embarrassment to the earlier miners, and it was thrown aside as worthless. Some of the old waste heaps are now being worked over for pitchblende. Since about 1830, it has been used for the extraction of uranium oxides, and in 1853 works were established by the Austrian Government for this purpose at Joachimsthal in Bohemia. The oxides were used in producing rich velvet-black, yellow, and orange colours in porcelain and enamels, and in the manufacture of the well-known fluorescent uranium glass. Limited amounts of the ore have also been used for the preparation of uranium salts employed as chemical reagents and in photography. A more recent application of uranium is in the manufacture of steel for guns.

The limited and uncertain nature of the deposits is well illustrated by the variations in the output of the pitchblende ore. In 1890, Cornwall and Bohemia produced 22 and 25 tons, and in 1897, 30 and 44 tons respectively. After the discovery of radium, the output increased to a maximum of 103 tons in 1905 in Cornwall, and of 52 tons in 1900 in Bohemia. Since then it has decreased to 6 and 8 tons respectively in 1909. Saxony produced only  $\frac{1}{2}$  ton in 1909. In Colorado, the output of pitchblende has varied between 4 and 20 tons per annum.

L. J. S.

#### PITTACAL *v.* WOOD, DISTILLATION OF.

**PITTIOSPORUM UNDULATUM** (*Vent.*). The fruit of this tree which is indigenous to South-Eastern Australia where it is known as 'mock-orange,' yields by distillation an oil of an orange-like odour and contains a large proportion of *limonene* besides small amounts of *pinene* and various esters and an optically inactive *sesquiterpene* (Power and Tulin, *Chem. Soc. Trans.* 1906, 89, 1083).

**PITURI.** The leaves of *Duboisia Hopwoodii* (F. v. Müll.), used as a narcotic (Brestowski, *Handwörterbuch Pharm.* 370). On distillation with steam was stated to yield an alkaloid, a colourless oil, b.p. 243°, called *piturin*. Rothera has shown, however, that the only alkaloid present is nicotine, which forms 2.67 p.c. of the leaves after drying at 60° (*Biochem. J.* 1910, 5, 193).

#### PIURI *v.* INDIAN YELLOW.

#### PLAGIOCLASE *v.* FELSPAR.

**PLANT-SPRAYS.** Spraying may be taken in a wide sense to embrace the application of solids, liquids, or gases to plants with the object of freeing them from insect or fungoid parasites, or of clearing them from dead bark, and such treatment may or may not interfere with the healthy functions of the plant.

#### SOLIDS.

Many liquid spray-fluids, or washes, contain solids in suspension, but it is only in a few cases that solids are used in the dry state; in such cases they are blown on to the plants by means of bellows, and the operation must be performed while the plants are wet with dew or mist, so that the solid may adhere to them. *Sulphur*, in the form of flowers of sulphur, is applied extensively in this way to hops for destroying mildew and red spider, and in certain other cases it is applied mixed with *lime*. The



nature of its action is at present obscure, but most probably depends on its being slightly volatile, for, when used in hot-houses, the most satisfactory results are obtained when it is painted on to the hot water pipes, or otherwise heated. At the same time its effectiveness is increased by the presence of moisture, though it hardly seems possible that the traces of sulphuric acid formed under such conditions can account for its action. Hellebore, consisting of the root-stock and roots of *Veratrum album* (Linn.) and *V. viride* (Ait.) is effective in destroying caterpillars on gooseberries, &c.: it acts chiefly by poisoning their food, but is probably also injurious to them by contact with their bodies. As it is less poisonous than arsenical compounds and loses its properties rapidly on exposure to air, it may be used with safety within a short time of the ripening of the fruit. Pyrethrum, obtained from the ground heads and stems of *Chrysanthemum* [*Pyrethrum*] *roseum* (Web. et Mohr) and *C. Marschallii* (Ait.) and *C. (Pyrethrum) cinerariifolium*, contains an oil which appears to act on insects only by contact. Besides being used in the dry form, it is used as a decoction and also as a fumigant.

#### LIQUIDS.

**A. Insecticides.** For a determination of the nature of the insecticide which is likely to be effective in any particular case, a knowledge of the life history of the insect is necessary to indicate at what period it is most vulnerable and by what means it may best be combated. Insects which chew the leaves are best dealt with by poisoning their food, whilst others which pierce the leaves and bark, extracting the juices from below the surface, are best attacked by the application of some corrosive substance to their bodies. The most effective procedure, where practicable, is to destroy the eggs of the insect: for this a corrosive substance is required, and such can only be applied to the plants while these are in the dormant condition. For facilitating insect eggs being reached by a fluid, as well as for reducing the number of crevices in which insects can deposit their eggs, the application of a detergent wash in the winter, to remove dead bark, moss, lichen, &c., from the trees is an important adjunct to an insecticide.

Many of the most popular insecticides and fungicides have come into use by accident, and although practical experiments have introduced considerable improvements in them, much uncertainty still prevails as to the method of their action; and it is remarkable that in very few cases has science provided satisfactory substitutes for these chance selections.

The chief classes of insecticides are (1) vegetable poisons consisting of alkaloids, (2) soft soap, with or without excess of alkali, (3) sulphur and sulphides, (4) phenol, (5) paraffin oil, (6) arsenical compounds, (7) lime.

(1) Of the vegetable poisons, *hellebore* and *pyrethrum* have already been mentioned, and these may be sprayed on to the trees in the form of a 3 or 4 p.c. admixture with water or dilute paraffin oil emulsion. If a decoction is used it should not be boiled. *Quassia* with soft soap is

much used for destroying aphids. The wash is made by boiling  $\frac{1}{2}$  to 3 lbs. of chips of the wood with 10 gallons of water, and adding  $\frac{1}{2}$  to 3 lbs. of soft soap.

*Nicotine* appears to be by far the most effective of the vegetable insecticides. A decoction of 'denatured' tobacco—which contains about 70 p.c. of tobacco mixed with sulphur, asafetida and flour—may be used, but owing to the great variation in the nicotine contents of tobacco, it is better to use nicotine itself. A solution of 0.075 p.c. is very effective for aphids, apple psylla, &c.: it is well to add to the solution 0.5 p.c. of soft soap.

It is noticeable that various alkaloids, such as aconite, hyoscyamine, nux vomica, &c., which are highly poisonous to vertebrate animals, have but little action on insects.

(2) *Soap* is generally used in connection with other substances as in the instances just mentioned, but it is also used effectively alone for killing certain aphides such as those attacking roses. It is probable that its action in such cases is due to its clogging the breathing apparatus of the insect: its low surface tension also enables it to wet bodies more effectively than other spray-fluids, though it may be remarked, a similar action in the case of saponin does not appear to increase the effectiveness of substances to which it is added. Soap is also largely used as an agent for emulsifying paraffin oil. In connection with this, and especially if alkali is added as well, it is used for the destruction of insect eggs, although its chief function under such circumstances is that of a detergent.

(3) *Sulphur* is generally used in the solid condition, as mentioned above, although it occasionally is made into a liquid wash with water and other substances. As an insecticide and still more as a fungicide, the *sulphides* play an important part. The origin of their use seems to have been the application to trees of a liquid used as a sheep dip, and known as the lime-sulphur-salt wash (California wash) or the lime-sulphur-soda-salt wash (Oregon wash). There are many recipes for making these, the more usual being to boil together for 45 minutes 3 to 6 lbs. of quicklime with 3 lbs. of sulphur, 3 lbs. of salt, and a limited quantity of water, the resulting liquid being afterwards diluted to 10 gallons. In the Oregon wash, about 1 lb. of caustic soda is added in addition to the above materials, and the heat generated on adding water to the mixture is sufficient to obviate the application of external heat. A wash of this strength can be used only on dormant trees, and is then more effective when applied hot; but at a lesser strength it is now being used on trees in leaf, chiefly as a fungicide. The wash always contains a considerable proportion of unaltered lime, the sulphur going into solution as calcium thiosulphate and pentasulphide. The latter undergoes rapid change, even in absence of air, the pentasulphide becoming converted into thiosulphate with the liberation of sulphur, and the thiosulphate into sulphite and more free sulphur: the sulphite ultimately oxidises to sulphate. Where caustic soda is used in its preparation, the sulphur reacts with it in preference to the lime. The method of operation of this wash is uncertain. It is used



habitually in the Western States of America for combatting San José scale, and according to certain experiments, none of the substances which it contains, when used separately, have any effect on the scale: according to other authorities, a mixture of potassium sulphide and lime is as effective as the wash. It appears that its action is in part mechanical, the sulphur deposited from it on to the trees glueing the scales to the bark and preventing the egress of the young insects. What function the salt performs is obscure, and according to some investigators it may be omitted without detriment. Owing to the excess of lime present in it and to the destructive action of sulphides on lichen, &c., the wash is a good detergent.

Lime and sulphur mixed with water without heating are sometimes used for aphids, mites, and red spider, being preferable to sulphur by itself; such a mixture always contains some products of the reaction of the two substances. Calcium sulphide solution is also used for the same purpose, but potassium sulphide is preferable, as soft soap can be added to it without causing decomposition: 3 to 10 ozs. in 10 gallons are the proportions recommended. It can also be mixed with an emulsion of paraffin oil.

(4) *Phenol*, either dissolved by itself in water, or with the addition of soap or glycerol, has been tried as a general insecticide without much success, but a solution of carbolie acid soap is very effective for certain aphides as well as mildews (e.g. of roses), and phenol figures as one of the ingredients of several proprietary insecticides which are now in use.

(5) *Paraffin oil* was used for spraying purposes very soon after it was first obtained. The undiluted oil cannot be used on trees, even in the dormant season, without some risk of injury, but injury does not always follow, even when the trees are in leaf, and it is a very satisfactory remedy to apply in cases (e.g. woolly aphid) where the eradication of a pest from a plantation is of more importance than the possible injury to some of the trees. In that case, a pneumatic sprayer should be used, which distributes the liquid in the form of a very fine mist. A good quality lighting oil must be used, higher boiling oils are certain to injure the trees, and so do the more volatile oils (petrol), due, probably, in the latter case to the cold produced by evaporation. Mixtures of oil and water, unless quite dilute, appear to do more damage than undiluted oils. The admixture of oil with water used to be effected by pumping the liquids from separate containers into one delivery hose fitted with a spraying nozzle. It is now more general to emulsify the oil in the water either by means of soft soap or of certain finely divided solids, such as the basic sulphates of iron or copper, obtained by precipitating the normal sulphates with lime-water or milk of lime. For plants in leaf, the proportion of oil should not exceed  $1\frac{1}{2}$  p.c., but where they are dormant 6 or 7 p.c. may safely be used. Much larger proportions are often used in America. For dormant trees it is usual to add to the emulsion  $2\frac{1}{2}$  p.c. of caustic soda, which makes the wash a powerful detergent, as well as an insecticide as regards the eggs of certain insects. In that case, a basic sulphate should

be used instead of soap as an emulsifying agent, although there are special brands of soap which act fairly well under the circumstances; those containing a large proportion of stearin yield a sufficient supply of small insoluble particles to prevent total de-emulsification when the potash soap is flocculated by adding the soda. Emulsions of paraffin may be used in conjunction with most insecticides and fungicides.

(6) *Arsenical compounds*. These supply some of the most powerful insecticides for leaf-eating insects. An aceto-arsenite of copper (Paris green), made by the action of arsenious oxide on verdigris, was one of the first of these substances to come into use, but it is liable to injure the foliage, the leaves becoming scorched, and often falling. This action is intensified if the Paris green contains excess of arsenious oxide, as it often does, and it is well to guard against this by the addition to it of an equal weight of lime. Calcium arsenite, made by boiling arsenious oxide with lime, is also used, although more frequently in the form of London purple, which is a waste product from dye-works and contains 75 p.c. of the arsenite. The compound which has come most into favour of recent years, chiefly on account of its causing very little leaf-scorching, is lead arsenate, also called gypsin, from its being first used for the gipsy moth caterpillar. When prepared by the action of lead acetate by sodium carbonate, or if the acetate to  $3\frac{1}{2}$  oz. of the crystallised, or to 2 oz. of the 'dry' arsenate for every 10 gallons) it consists of the triplumbic salt,  $Pb_3(AsO_4)_2$ , but when lead nitrate is used, the product consists chiefly of  $Pb_2H_2(AsO_4)_2$ . Both substances are slightly soluble, the latter being the more soluble of the two, and they are in a fine state of division which facilitates their distribution over, and adherence to, the leaves. The insecticide is sold in the form of a paste, mixed sometimes with other materials, and is preferable to the home-made material, inasmuch as it is free from the acetic acid which is liberated in the home-made material, and tends to cause leaf-scorching.

(7) *Lime* has been used of late years together with salt, as an insecticide in special cases (apple psylla). The lime-salt wash is made by slaking 15-20 lbs. of lime, adding 2-3 lbs. of salt,  $\frac{1}{2}$ -1 lb. of water-glass, and making up to 10 gallons. It is applied to the trees, as hot as possible, a few weeks before the buds open. The wash appears to act partially by destroying the eggs and partially by glueing them up and preventing the egress of the insects. What function the salt performs it is difficult to see. Strong brine will destroy insect eggs by depleting them of their liquid contents, but the salt is hardly present in this wash in sufficient proportion for such an action.

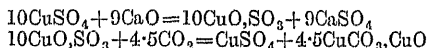
B. *Fungicides*. Sulphur, and the sulphides previously described, are important fungicides, the latter being of special use in the case of surface moulds or mildews. Phenol and the salts of iron appear to have but very feeble fungicidal properties, and mercuric chloride, although of great value in the laboratory, has not been successfully applied to plants. By far the most important fungicide appears at present to be copper, and it has been applied in a great variety of forms.

The problems of fungicidal action are complex and, at present, very obscure. A fungus destroys its host-plant by the development of mycelium, or thread-like roots, which penetrate and break up the plant cells. As these do their work within the body of the plant, they cannot be reached by any fungicide. Remedial measures must depend on killing the spores or seeds of the fungus, or else on protecting the plant in such a way that fungus spores alighting on it will find conditions unsuitable for germination. The fungus being, like its host, a living organism, deleterious to it is likely to be deleterious to the host-plant also, and a scorching action on foliage has been found to be a general concomitant of fungicidal action, although under certain weather conditions such damage does not take place. When a plant is in the dormant condition and a strong fungicide can be used on it, the fungus also exists in the form of resting spores which are very resistive to treatment.

For a substance to be operative it must either be soluble to start with or become soluble during use. The insoluble copper compounds used as fungicides apparently become soluble by the agency of carbon dioxide, copper sulphate being the substance liberated; and the evidence at present seems to be against the view that anything excreted by the fungus itself or by the host-plant acts as a solvent agent. Fungus spores, while actually germinating, or the mycelium while in a state of activity, would doubtless excrete substances capable of dissolving copper compounds, and the leaves of some trees (e.g. the lime), certainly do so, as do the leaves of many other trees when bruised; but no such action has yet been established, either with dormant fungus spores or with the sound leaves of fruit trees. The protective action of a fungicide consists in its forming a coating on the leaf, generally of copper carbonate, which is slightly soluble and which, therefore, prevents fungus spores from germinating there. But protection may also occur through the inhibition of soluble copper into the substance of the leaf itself, for it has been shown that copper is thus absorbed, becoming apparently substituted for the iron which is normally present therein. It appears that both the fungicidal and the scorching action of soluble copper compounds is dependent solely on the amount of copper contained in them, unless the acid radicle present has a fungicidal action of its own, and the intensity of the effect is approximately a logarithmic function of the amount of copper. Often very little is gained by a considerable increase in strength.

The use of copper compounds originated in verdigris having been applied to roadside vines to prevent depredations, with the result that such vines were found to remain free from mildew. This led to the use of copper sulphate, to which lime was next added to neutralise the acid which was supposed to be responsible for the scorching produced. Such a mixture was known as Bordeaux mixture, and it is still the most extensively used fungicide. The proportions of ingredients recommended have varied largely at different times, but at present it is generally made with 8 lbs. of lime and 8 lbs. of copper sulphate to 10 gallons, and it is

obtained in the most satisfactory state of subdivision by adding the sulphate in the form of a strong solution to the lime, previously slaked and mixed with the bulk of the water. The action of lime on copper sulphate results in the formation of a series of basic salts, of which  $4\text{CuO}\cdot\text{SO}_3$  is the lowest, and is that formed when the lime is just sufficient to precipitate the whole of the copper. When the amount of lime is increased until the liquid becomes barely alkaline, the compound formed is  $10\text{CuO}\cdot\text{SO}_3\cdot 2\text{CaO}$ , which is a very bulky substance in the liquid, and very unsuitable for spraying. With a still larger proportion of lime, such as is used for Bordeaux mixture, it is the latter body which is formed at first, as the water present is insufficient to allow the whole of the lime to react at once, but this excess of lime gradually dissolves and the precipitate is converted into another compound,  $10\text{CuO}\cdot\text{SO}_3\cdot 2\text{CaO}$ , mixed with copper cuprite, this mixture forming a violet blue compact precipitate, little suited for spraying. Bordeaux mixture should, therefore, be used as soon as possible after preparation. Most of the basic sulphates are insoluble, but are decomposed by carbon dioxide reproducing copper sulphate, but only in amounts representing a small proportion of that used in making them, as is evident from the equations:



although the proportion liberated in this state is found to be considerably in excess of that here indicated, the additional  $\text{SO}_3$  required for the production of the excess being derived from the calcium sulphate, which is not present as such, but as an integral portion of the basic sulphate itself. The copper sulphate liberated acts directly as a fungicide in the manner above indicated, whilst the copper carbonate formed supplies a protective coating to the leaf. With ordinary Bordeaux mixture there is considerable excess of lime present, which decomposes any sulphate as soon as it is formed, the practical result being that only 2 or 3 p.c. of the copper sulphate taken to make it becomes converted again into sulphate, whereas about twenty times that proportion is obtained when pure  $10\text{CuO}\cdot\text{SO}_3$  is used, but the reduction in the proportion of active fungicide in the case of the ordinary mixture is partially counterbalanced by an increase in the protective carbonate formed. With ordinary Bordeaux mixture it is only when the deposit dries up and liquid communication between the lime and basic sulphate is cut off that the copper sulphate is liberated. The carbon dioxide which is evolved cannot remain very long as such on the leaves for it is gradually converted into carbonate by the calcium carbonate present.

It has been shown that carbon dioxide at the low pressure at which it normally exists in the air, does not react with the basic sulphates so as to liberate permanently the amount of copper sulphate indicated in the above equations; but carbon dioxide is evolved in large quantities from foliage, and the reaction actually occurring probably approximates to

that indicated. Judging by the fungicidal results, the proportion of soluble copper liberated from the compound  $10\text{CuO}\cdot\text{SO}_3$  is six to twelve times that liberated from ordinary Bordeaux mixture. The weight of copper, instead of being as much, as experiments with p. suggested. This superior efficiency of  $10\text{CuO}\cdot\text{SO}_3$  has led to its introduction on to the market in the form of a paste. The absence of solid particles of lime which clog the spray of the labour of horticulturists claimed for it; but important advantage probably consists in the reduction of the amount of copper distributed over the land by the spraying. Seedling plants are remarkably sensitive to the toxic action of copper, the effect of one part of the metal in 10,000,000 of water being recognisable on barley seedlings. Copper carbonate is soluble in rain water to a much greater extent than this, and the amount of copper reaching the soil in a single spraying would be sufficient to convert the soil-water in the upper nine inches into a solution containing enough of the metal to render it markedly toxic. So far as casual observations go, no deterioration of soil has been observed as a consequence of Bordeaux spraying, indicating that the ultimate compound of copper and metal must be a body less toxic than carbonate, but until more is known on the subject it is eminently desirable to diminish the accumulation of copper in the soil as much as possible. Herbage under trees may also become poisoned by copper spraying. Former experiments on this point had indicated that no such danger existed, but an instance has occurred in which a large number of sheep were killed by copper poisoning in a grass orchard which had been sprayed. Fruit should not be sprayed with copper within 5 or 6 weeks of its ripening.

Various dried Bordeaux mixtures are in use as substitutes for the ordinary mixture. They consist mainly of the basic sulphate  $4\text{CuO}\cdot\text{SO}_3$ , and generally contain some soluble copper. The amount of soluble sulphate liberated from them by the action of carbon dioxide is much less than that indicated by their composition, the comparatively large particles of which they are composed becoming encased in the carbonate formed, thus preventing the completion of the action. They are comparatively dense powders, which renders them inferior as spraying materials.

Copper carbonate itself is sometimes applied direct to the trees, as a substitute for Bordeaux mixture, and is known as soda Bordeaux. It is made by mixing 1.84 lbs. of crystallised sodium carbonate with 1 lb. of copper sulphate to make 10 or 20 gallons of wash. The precipitated carbonate consists of  $5\text{CuO}\cdot 2\text{CO}_2$ , some of this (to the extent of 0.003 p.c. of copper) remaining dissolved, while more copper is found in solution, if either a smaller or larger proportion of sodium carbonate is used, a cupric carbonate being formed in the latter case. The precipitated carbonate soon becomes granular and compact, changing into malachite,  $2\text{CuO}\cdot\text{CO}_2$ , so that the wash should be used at once after being made. The large amount of copper contained in it is a disadvantage, and the acid sodium carbonate, present as one of the products

of the reaction, is liable to injure delicate foliage.

The addition of treacle to Bordeaux mixture has been advocated as a means of rendering some of the copper soluble and also of increasing its adhesive properties. If the mixture is made with pure materials, the copper present dissolves in the dextrose of the treacle, either entirely or partially, according to the proportions, to give a violet solution which begins decomposing almost at once with the liberation of cuprous oxide. Such a mixture may either be very rich in dissolved copper or may consist of nothing but cuprous oxide, and is clearly very unsuitable for a spray fluid.

Numerous other copper compounds have been tried as substitutes for Bordeaux mixture, but without much success. Several of them are cuprammonium compounds which present difficulties in preparation of definite strengths, and there is much risk with them of the ammonia injuring foliage. Copper sulphate itself may be used, up to a strength of 0.25 p.c. copper, on trees while dormant.

**C. Detergent washes.** Lime-washing the trunks and main branches of trees has long been practised as a means of destroying scale and reducing insect attacks. The use of caustic soda for the lime produces more satisfactory results, and permits of the whole tree being treated by spraying. A wash containing  $2\frac{1}{2}$  p.c. of caustic soda is recommended, and its efficacy is further increased, both as a detergent, and still more as a direct insecticide, by the addition of about 6 p.c. of paraffin oil, this being emulsified with it by the agency of the basic sulphates of iron or copper. A recipe, the origin of which is unknown, is very widely circulated, in which about half of the above quantity of caustic soda is supplanted by an equal weight of potassium carbonate; but it has been proved that the latter is practically valueless as a detergent, and the use of it merely entails loss of money and efficiency.

#### GASES.

Hydrocyanic acid is used in the fumigation of hot-houses for the destruction of plant lice, &c.; it is also used in many countries for disinfecting imported nursery stock, and in California it is applied to peach trees in plantations for scale, each tree being covered with a tent during the operation. To avoid danger to the operator, potassium cyanide is wrapped up in paper, and lowered from outside by means of a string into a jar of dilute sulphuric acid. This is not always satisfactory, as the paper sometimes becomes converted into parchment paper and the cyanide becomes coated with potassium sulphate, which arrests the action. A better method is to enclose the cyanide in a little zinc canister made for the purpose and place the whole in the acid. For each 100 cubic feet of space,  $\frac{1}{2}$  to  $\frac{3}{4}$  oz. of 'lump' potassium cyanide is used, and for each ounce of the cyanide, one liquid ounce of acid previously diluted with 3 to 4 ounces of water. 'Stick' cyanide contains only 40 p.c. of potassium cyanide, and larger quantities of it must be used. Potassium cyanide is taken (which is preferable on account of its

being more easily soluble), the above quantities must be reduced by 25 p.c. Hydrocyanic acid is liable to cause some injury to young plants, and in fumigating these they should not be exposed to the direct stream of gas as it ascends from the generating vessel. Its action in destroying insect eggs is somewhat uncertain, and in the case of green-houses it is often necessary to repeat the fumigation after a fortnight's interval, to destroy insects which have hatched out from the eggs. For freeing nursery stock from woolly aphis, an advantageous substitute for fumigation is to immerse the trees bodily in water at 115°F. for 10 minutes.

Sulphur, as already mentioned, probably acts as an insecticide owing to its volatility, and it is often used for fumigating houses by heating it, taking care not to let it catch fire. Smouldering tobacco and pyrethrum are used in the same way.

S. P. U. P.

**PLASMION.** Milk casein made soluble by alkalis.

**PLASTER OF PARIS** *v.* CALCIUM.

**PLASTIC CLAY** *v.* CLAY.

**PLATINOTYPE PROCESS** *v.* PHOTOGRAPHY.

**PLATINUM.** Sym. Pt. At.wt. 195.2. In the group of the platinum metals are included platinum, iridium, rhodium, palladium, ruthenium and osmium. They are almost entirely obtained from the crude 'platinum' which, originally present in traces in the older plutonic rocks, has become concentrated in the alluvial deposits derived from their disintegration.

The crude platinum is found in these alluvials as water-worn, rounded or flattened grains or nuggets or, very rarely, as cubes or octahedra, together with brighter, almost micaceous flakes of the alloy of iridium and osmium known as osmiridium or iridosmine. True nuggets are extremely rare, although one from the Urals, weighing over 250 oz., is exhibited at the Demidoff museum in St. Petersburg, and one weighing about 24 oz. has been found in Colombia. Platin-iridium, an alloy of platinum and iridium, practically free from osmium, is also commonly associated with the ordinary crude platinum, while native palladium occurs with it in the Republic of Colombia, the Harz, &c., and in copper-nickel ores in Ontario, Wyoming, &c.

Chromite, magnetite, ilmenite, and other heavy minerals which occur in serpentines and other alteration products of the parent rocks, are also found together with gold, in association with the crude platinum, but it is curious that, although gold and tin commonly occur together in alluvial deposits and, like the rare minerals tantalite, columbite, molybdenite, monazite, &c., are derived from plutonic rocks similar to those yielding platinum, they do not commonly occur in alluvials which are sufficiently rich to be worked for that metal.

Platinum occurs in minute traces in most river beds the sands of which come from the older rocks, and has been found in dolomite, barytes, wollastonite, and many other rock-forming minerals produced by the metamorphism of such rocks, and in the metalliferous minerals associated with them. The presence of copper and iron in alloy with platinum in most varieties of crude platinum from the most widely separ-

ated districts is interesting, and the fact that it has been found in meteoric iron with nickel and in the cupriferous nickel ores of Sudbury in Ontario is deserving of special mention. The actual commercially workable sources of platinum are extremely limited, and there is no reason to anticipate the discovery of any new fields which are likely to add materially to the production except as by-products from smelting operations.

Crude platinum commonly contains sufficient iron to be magnetic, so that it may be separated roughly from osmiridium by a carefully regulated separator, but the danger of removing platinum with the magnetic or slightly magnetic iron sands, &c., which would require to be first removed from roughly dressed alluvial by a comparatively weak magnet, is likely to prevent the use of electro-magnetic separators on a commercial scale.

As platinum does not amalgamate with mercury, the removal of native gold from native platinum is a simple matter, but this very fact results in the loss of much of the latter metal in alluvial workings where platinum occurs in small proportion as compared with the gold and is, in too many cases, allowed to pass away with the waste from the amalgamation. It is impossible to estimate the extent of this loss, but it is a fact that increasing proportions of platinum and the allied metals are being recovered in the refining of bullion obtained from alluvial gold, and that all ordinary refined gold contains platinum and iridium. From this source and from the treatment of the matte from the smelting of the ores of the Sudbury-arsenide, where the

PtAs<sub>2</sub>) occurs with nickelerous pyrrhotine—of the copper ores of Wyoming, and of the ores of lead and silver which commonly contain platinum in traces, a considerable increase in the production of the platinum metals may be hoped for; but there is no reason to expect any material increase over the present alluvial output, and no ore *in situ* rich enough in platinum to justify direct treatment for its recovery, has yet been discovered. The fact that platinum cannot be amalgamated with mercury or profitably extracted by alkaline cyanide, renders it impossible to treat platiniferous ores similarly to gold ores, even if they occurred to the same extent and were of the same richness as the latter. In this connection, it may be stated that the United States Geological Survey Report on the Production of Platinum, &c., for 1910, estimated the production of platinum in the United States from the refining of bullion in 1910, as about 500 oz., a large increase on the recovery from that source in 1909.

Selected platiniferous nickel ore from Sudbury and the copper-nickel matte obtained from the smelting of the ore, have been treated by the Port Orford Copper Company in the United States and by others, for the extraction of platinum and the allied metals, and there is good reason to hope that a substantial increase in their production will be obtained from this and similar sources.

It is impossible to state the statistics as to the total weight of platinum either

crude or refined platinum. The official figure for Russian production of crude platinum in 1910 is 175,716 oz., but it is stated that the actual production was about 275,000 oz. and it has even been given as over 300,000 oz. In other countries, the statistics commonly include much old platinum which has been worked up, while, in some cases, part of the official figures are for real platinum and others for crude, *i.e.* for raw alluvial concentrate yielding anything between 60 p.c. and 80 p.c. of platinum with perhaps 10 p.c. of other metals of the platinum group.

The following figures issued by the United States Geological Survey in November, 1911, include probably the most accurate estimates of the production of the principal producers in 1909 and 1910. The production is given in troy ounces of crude platinum (which may be taken as roughly containing 70 p.c. of platinum), except in the case of the United States matte

and bullion, where the figures given naturally refer to refined platinum:—

	1909	1910
Russia . . . . .	264,000	275,000
Republic of Colombia . . . . .	6,000	10,000
United States, domestic crude . . . . .	672	390
United States, from foreign and domestic matte and bullion . . . . .	600	1000
Borneo and Sumatra . . . . .	500	200
New South Wales . . . . .	440	332
Canada . . . . .	30	30
	272,242	280,952

The following analyses are sufficiently typical to indicate the general character of crude platinum, &c., from various localities. They are somewhat old (the first five being by Deville and Debray) and the ruthenium has been ignored except in the case of the osmiridium, but they are probably as trustworthy as any which have been published:—

—	Pt	Ir	Os	Rh	Pd	Ru	Au	Cu	Fe	Osmiridium	Sand
<i>Crude Platinum</i>											
Choco (Colombia) . . . . .	86.2	0.85	—	1.40	0.50	—	1.00	0.60	7.80	0.95	0.95
California . . . . .	85.5	1.05	—	1.00	0.60	—	0.80	1.40	6.75	1.10	2.95
Australia . . . . .	79.85	4.20	—	0.65	1.95	—	0.55	0.75	4.45	4.95	2.69
Urals . . . . .	61.40	1.10	—	1.85	1.80	—	1.20	1.10	4.55	26.00	1.20
Urals . . . . .	76.40	4.30	—	0.30	1.40	—	0.40	4.10	11.70	0.50	1.40
(Nischnei-Tagilsk) . . . . .	75.10	2.60	2.30	3.50	1.10	—	0.40	1.00	8.10	0.60	—
Borneo . . . . .	70.21	6.13	1.15	0.50	1.41	—	—	0.34	5.80	—	—
<i>Platin-iridium</i>											
Urals . . . . .	19.64	76.85	—	—	0.89	—	—	1.78	—	—	—
Brazil . . . . .	55.44	27.79	—	6.86	—	—	—	3.30	4.14	—	—
<i>Osmiridium</i>											
Urals . . . . .	10.08	55.24	27.23	1.51	trace	5.85	—	trace	trace	—	—
California . . . . .	—	53.50	43.40	2.00	—	0.50	—	—	—	—	—
Australia . . . . .	—	58.13	33.46	3.04	—	5.22	—	0.15	—	—	—

The purest nugget yet analysed contained 86.5 p.c. of platinum. They usually contain between 70 p.c. and 85 p.c., iron being the principal impurity, although copper is invariably present. In one nugget from the Urals, 19.5 p.c. of iron has been found.

Crude platinum is separated from alluvials by ordinary hand sluicing or dredging operations, and may be regarded as a by-product in gold dredging in the United States, Canada, Colombia, and many other districts, and as the main product in the Urals which, from five districts, is stated to produce about 95 p.c. of the world's output. In the Urals, about 80 p.c. of the total yield is at present obtained by hand sluicing, but dredging is likely to largely supplant hand work in the near future.

The metal occurs in an eroded peridotite covering a large area, but, although increased activity has arisen through the rise in the price, production is almost stationary, and any increase must be dependent upon dredging operations dealing with deposits too poor to permit of treatment except on an enormous scale and under more economical conditions. A large proportion of the total production is smuggled across the frontier, and it is believed that the officially certified output of 176,716 oz. of crude platinum for 1910, should be increased

by at least 100,000 oz., to allow for such illicit and other additional production.

It has been stated that the alluvial treated in Russia averages between 30 and 35 grs. of crude platinum per ton, but this probably refers to the material actually washed by hand labour and ignores the overburden which has first to be removed. It is probable that the material actually handled averages under one-third of that amount, or well under one part per million.

Apart from Russia, the most important producer is the republic of Colombia which in 1909 yielded, from two districts on the Pacific side of the state, about 6000 and, in 1910, about 10,000 crude ounces. The output of platinum in Colombia is, however, so small in comparison with the gold, which constitutes the main value of the alluvials, that the industry has not hitherto been regarded of especial importance, although the total production to date is stated to have exceeded half a million ounces of crude platinum and although platinum was obtained from Colombia or, at any rate, from South America, nearly a century before it was discovered in Russia.

In 1819, grains of a white metal were found in the auriferous gravels of the Urals, and in 1823, the metal was proved to be platinum.

From 1825 to 1845, the Russian Government absorbed all the output for their coinage but in that year such coinage was discontinued, and a heavy fall occurred in the price previously commanded by Colombian platinum and, until recently, platinum has only been produced in South America by natives operating with the crudest appliances and only when necessity compelled them to work.

The platinum industry is practically controlled by three firms, Johnson, Matthey and Co., of London; Heraeus and Co., of Hanau; and Quennessen de Belmont, Legendre and Co., of Paris, who purchase and refine practically all the Russian output and a large proportion of the small quantity produced elsewhere. It is true that two firms in St. Petersburg refine between 6000 and 10,000 oz. yearly, and that between 5500 and 6000 oz. is obtained yearly in the United States from home and imported crude ore, matte and bullion, but the whole forms an extremely small proportion of the world's output of nearly 300,000 oz. The

are present in recovery, and high market value, is entirely dependent on the amount of crude platinum obtained by the miner or concentrated by the skill with which it is treated by the metallurgist.

It is interesting to note that Johnson, Matthey and Co., who introduced autogenous soldering with the oxy-hydrogen blowpipe and who are still the largest refiners of the metal, were the first to engage in the industry as a commercial enterprise and have throughout been the most active in introducing improvements in the metallurgical and chemical treatment of crude platinum, in producing the various platinum metals in a state of purity or as alloys of definite composition and for special uses, and in the development of both the commercial and scientific industries. From the point of view of the analyst and physicist, probably no rare metals are of such importance in their work or so difficult to obtain in a condition suitable to their requirements.

At the close of the eighteenth century, Marggraf, Achard, and others prepared a platinum crucible by igniting an alloy of platinum and arsenic, and hammering up the mass of malleable platinum thus left and, for some years from 1787, Jeanety, a working silversmith, employed the method commercially in Paris. The metal was, however, very impure. It failed to withstand high temperatures and was unsatisfactory for the fusion of alkaline carbonates. The precipitation of the double chloride of platinum and ammonia, and the presence in it of the red iridium salt, were known even at that period, and Count Puschkin, Vice-President of the Department of Mines of St. Petersburg, referred to it in 1797 as well known and, at the same time or a year or two later, suggested the use of the precipitate as a means of preparing pure platinum after first converting it into an amalgam with mercury.

Between the years 1800 and 1808, Thomas Cook, a relative of a grandson of the founder of the firm of Johnson, Matthey and Co., elaborated the method of dissolving the crude metal in *aqua regia*, precipitating it as the double

chloride of platinum and ammonium, and igniting the washed precipitate to spongy platinum under conditions which render it suitable for being hammered and worked up into crucibles, &c. This process, which was afterwards commonly known as Wollaston's, on account of his having described it, with many details, in the Bakerian lecture for 1828,

is in many works on Chemistry, and is the basis of all present methods of refining platinum. The platinum thus obtained may contain as much as 2 p.c. of iridium with traces of other of the platinum metals, and is at least as pure as the platinum obtained by the Wollaston process.

The treatment, contain osmiridium, and various impurities, such as chromite, zircon, spinel, &c., originally present in the crude platinum, while the mother-liquor from the double platinum-ammonium precipitate contains most of the rhodium, palladium, and ruthenium, together with a small proportion of the iridium and osmium. The insoluble matter and the mother-liquor are both worked up for the separation of these metals, as stated later.

The important and increasing production of the platinum metals through concentration during the 'bessomerisation' of the matte obtained from the nickel-copper ores of Sudbury, Ontario, and from the arsenical cobalt nickel ores, associated with native silver in the Cobalt district of Ontario, has already been mentioned. These and other metallurgical operations in which the precious metals become naturally concentrated in a product requiring but a small amount of acid treatment, are the only ones in which any substantial increase in the output can be expected, but they are sufficiently promising to deserve special attention from both metallurgist and chemist. No trustworthy information is available as to the exact procedure, but it appears to be mainly confined to the treatment of the anode mud obtained during the final electrolytic purification of the metals or the residue left by the acid or other treatment of the matte. The 'mud' or residue contains the gold, silver, and platinum metals together with selenium, bismuth, &c., and is melted down and refined by ordinary chemical processes.

In 1910, over 2100 oz. of palladium, in addition to 1000 oz. of platinum and an unknown amount of iridium, rhodium, and ruthenium, were produced in the United States from the treatment of bullion and matte, the latter of which was largely obtained from the Ontario ores.

Platinum is a tin white metal, harder than copper, capable of taking a high polish and, when pure, ranking next to gold and silver in malleability and ductility. Its sp.gr. is 21.46 (G. Matthey). It melts at 1710°-150° as determined with a resistance pyrometer by Harker, or at about 1753° as determined with the optical pyrometer by Wardner and Burgess. It is stated by Knooeke to commence to volatilise *in vacuo* at 540°, while, according to Hulett and Berger, volatilisation commences at 500° in air, but does not occur in the absence of oxygen. The extent of such volatilisation is, however, still doubtful and, under normal conditions, is

a matter of only slight technical importance, except in so far as it emphasises the necessity for cleanliness of utensils and special care in the method of heating and in ensuring perfect combustion of the fuel. The loss experienced with pure platinum vessels at the strongest heat to which they are subjected, is known to be negligible, and the other platinum metals, in the electric furnace.

The expansion of platinum when heated, is less than that of any other single metal, its coefficient of linear expansion being  $\cdot 00000907$  at  $50^\circ$  according to Fizeau, or  $\cdot 00001130$  at  $1000^\circ$  according to Le Chatelier. This expansion being about equal to that of ordinary glass, has resulted in the use of platinum for a large variety of electrical purposes, and there is a constant increase in the gross consumption for the leading-in wires of electric lamps, although improvements in the construction of the lamps themselves have resulted in less platinum being employed per lamp. For the same reason, *i.e.* because its expansion is about equal to that of the material of which the best artificial teeth are made, very large quantities of platinum are used in dentistry, in addition to its employment in alloy with silver. Its high melting-point and great electrical resistance, and the absence of oxidation, render it the best medium for localis current in where efficiency and convenience are more important than saving in cost.

Although the most useful of all metals for general scientific purposes, it is attacked by many reagents which would scarcely be expected to have any action upon it, and the greatest care is essential in its use. Practically all other metals will alloy with it, and all—excepting certain of the other platinum metals—lower its melting-point. For this reason, no metal or metallic compound should

sulphides, or arsenides, or arsenates or phosphates (in presence of a reducing agent or, practically speaking, under any circumstance) be heated in it. Caustic alkalis or alkali nitrates or the alkaline earths or peroxides or per-salts generally should also not be fused in it, as they attack and partly dissolve the metal as well as tend to render it permanently brittle.

The action of many salts and mixtures of salts on platinum is somewhat obscure. Fused ammonium sulphate or the halogen salts of the alkali metals have little or no action upon it, but a mixture of this sulphate with ammonium or potassium bromide, corrodes it rapidly. The alloys of platinum and iridium are more resistant to ignition and to corrosion, &c., by reagents than pure platinum, but it is stated that platinum vessels containing 3 or 4 p.c. of iridium are more liable than pure platinum to form a covering of soot from illuminating gas and to be more corroded thereby. The necessity for care in ensuring perfect combustion when using water-gas or gas containing carbon-monoxide, is well known, although the cause is not clear. It may possibly be due in some degree to the presence of iron carbonyl as well as to the imperfect combustion of the carbon monoxide.

The power of platinum (referred to later) occlude gases, has doubtless much to do with the brittleness which the metal acquires if used without due care and without frequent burnishing to overcome the porosity which, at first only superficial, gradually extends to the interior, if not overcome by frequently rubbing down the surface. Acid salts and pure unmixt acids are practically without action upon it and the demand for platinum for sulphuric acid concentration has accounted in the past for the locking-up of more of the metal than any other use. The first large piece of platinum apparatus for this purpose was made by Messrs Johnson, Matthey and Co. It was capable of holding 300 lbs. of sulphuric acid and was employed over a hundred years ago by Sandma in the Borough. Since the Paris Exhibition of 1855, when the makers exhibited a gold-line platinum still, Mr. J. S. Sellon, one of the directors of the firm, has superintended the manufacture of hundreds of stills aggregating nearly 50,000 oz. in some years.

Of late years platinum has been largely replaced in sulphuric acid concentration by gold, and, more recently, by silica-glass or where the presence of traces of iron is unimportant, by vessels of specially resistant alloy of iron and silicon, such as 'tant-iron.' Its use in dental alloys, although always large, become substantially reduced when the price rises, so that much of the metal which would otherwise become permanently locked-up, is released for other uses; while the employment of platinum and its alloys for self-lighting lamps—an extremely old use which became again fashionable during the last decade—has apparently been finally given up in favour of spirit lamps ignited by the spark from an alloy containing cerium.

On the other hand, platinum black as a catalysing agent (as referred to later) in the manufacture of sulphuric acid, is used so rapidly and is causing the consumption of a large quantity of the metal; while its use in electro-chemistry and pyrometry and in the sparking plugs of explosion engines, and the collectively large and constantly increasing use of small pieces of platinum apparatus, add largely to the demand.

Perhaps the most serious and almost permanent loss of platinum is in the enormous consumption in dentistry, which is stated to account for over 60,000 oz. annually. An increasing amount is used in jewellery, and at least two-thirds of the large quantity employed in the lamp and other electrical industries is permanently lost. The process of dissolving platinum in aqua regia, and the salts in the manufacture of pottery, &c., also account for an increasing and very considerable permanent loss of the metal.

The power of absorbing gases, possessed by platinum, has found a number of both purely scientific and practical applications. Although platinum is not porous, it is a powerful absorbing gases and is even porous to them, the value of the metal in this connection is mainly seen when it is in the form of spongy platinum or platinum black. Solid platinum will absorb 3.8 volumes of hydrogen gas at a red heat, and the gas will pass through platinum tubes at bright



redness. The fact that many other gases and vapours are similarly adsorbed or occluded by this metal, has been taken advantage of in the glow-lamp of Davy and the lamp of Döbereiner. In each, the simultaneous occlusion of a combustible gas or vapour and oxygen from the air, brings the two into such intimate contact as to induce immediate combination. The heat of the combustion in the 'pores' of the metal, causes incandescence of the wire spiral in the case of the lamp of Davy or of the platinum sponge in the Döbereiner lamp.

By careful adjustment of the conditions, either complete or partial oxidation may be attained, and many oxidation processes may be carried out automatically with suitably prepared platinum. One of the earliest to be tried on the commercial scale was the conversion of alcohol into acetic acid.

The preparation of platinum sponge and platinum black for catalytic purposes, requires care and experience. For the manufacture of the former, the double chloride of platinum and ammonium is ignited to drive off the ammonium chloride and the chlorine combined with the platinum at the lowest possible temperature, so that the sponge shall retain the maximum surface; or asbestos, pumice, or other porous material may be saturated with platinum chloride and ignited, so that a still larger surface is exposed. Platinum black, a far more active form of the metal, is obtained as a finely divided residue, by treating alloys of platinum and soluble metals with dilute acids; or, better, by precipitating the platinum from a weak solution of the chloride with a reducing agent. Platinum black is capable of absorbing over 800 times its volume of oxygen, a portion of which appears to enter into combination as platinum hydroxide. It forms an extremely powerful oxidising or catalysing agent and is frequently used as such in organic chemistry, but it rapidly loses a portion of its activity and becomes denser and of the nature of spongy platinum.

The only large scale catalytic process in which platinum is employed, is the 'contact' process, in which sulphuric acid is manufactured direct from a mixture of sulphurous acid gas and air. This process, although long known, was not employed commercially until a demand arose for the strongest possible sulphuric acid for the manufacture of dyes, explosives, &c. The cost of evaporating the weak acid from the lead-chamber process or of preparing Nordhausen acid, and the increasing requirements of the trade led, however, to such improvements that 'contact' acid can be obtained of any necessary strength in terms of  $\text{SO}_3$  dissolved in  $\text{H}_2\text{SO}_4$  (v. SULPHURIC ACID).

The difficulties due to the rapid falling-off in the activity of the spongy platinum employed as the catalyser, have now been largely overcome, and the working up of the exhausted metal into fresh sponge has been simplified. The fact that arsenic rapidly 'sickens' the platinum, has rendered it necessary to remove that impurity from the sulphurous acid gas before oxidation, and the success which has attended such treatment has resulted in the production of acid remarkably free from arsenic and, at the same time, allowed the use of pyrites more arsenical than was previously permissible.

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Such purification is largely effected by the use of iron oxide which, while removing arsenic with formation of ferric arsenate, oxidises much of the sulphurous acid. Many other catalysers have been employed with success, but none result in so complete a conversion of the sulphur dioxide into the trioxide and, even when they are employed, the aid of spongy platinum is generally required for the completion of the reaction.

The electrolytic action induced by the presence of a minute trace of platinum has a remarkable effect in promoting the solution of many metals in acid or other solvents, and in increasing their activity as reducing agents, &c. As platinum is so readily reduced by metals, the addition of a few drops of platinum chloride to the solution in which the metal lies, will often suffice for a large quantity of metal at a negligible cost, so that the application of this property which, although well known, has not yet been commercially employed, is well deserving of attention.

Although platinum can be readily alloyed with most metals, the alloys of industrial importance or even of scientific interest are few. As a rule, the qualities which render platinum valuable in the arts are destroyed by the addition of other metals, even in small quantities, and the addition of small quantities of platinum to other metals results in no improvement. The alloys of gold and platinum are of little importance, although of considerable interest on account of the fact that all bullion contains at least a trace of platinum, and that bullion is now largely treated electrolytically for its recovery in the United States and Germany. An alloy containing 70 p.c. of gold and 30 p.c. of platinum is only slightly yellow while, when more than 35 p.c. of platinum is present, no sign of yellow colour appears. Platinum and other platinum metals have a curious tendency to separate from their gold alloys, a fact which is noticeable when assaying gold bullion, where iridium, even when present in traces only, tends to pass to the bottom of the gold bead during cupellation. Matthey has pointed out that platinum concentrates towards the centre of an ingot cast from gold platinum alloys, so that great difficulty is experienced in the sampling of platiniferous bullion such as is obtained from many alluvial gold concentrates.

The platinum-silver alloys are of interest on account of their use in dentistry and, to some extent, as a solder for platinum, but mainly because the solubility of platinum so alloyed in nitric acid, and the insolubility in sulphuric acid, are utilised in the separation of platinum from gold and in the assay of ores supposed to contain platinum. For the latter purpose, an ordinary fire assay is performed exactly as for a gold ore, so that the platinum becomes collected in a button of lead together with any gold and silver which may be present. After the lead has been removed by cupellation, the silver may be removed (leaving the gold and platinum) by heating with sulphuric acid diluted with about one-fifth of its volume of water, or both the silver and platinum may be entirely dissolved (leaving the gold), by heating with dilute nitric acid. To ensure



complete solution of the platinum in nitric acid, not less than 10 parts of silver to 1 of platinum must be present.

The alloys of platinum and iridium are of great value and of increasing importance. The presence of even a small quantity of iridium in platinum increases its hardness and generally adds to its resistance to heat and to corrosion by reagents. The alloy containing 10 p.c. of iridium has exceptional properties in these respects, and has been employed in the manufacture of standard weights and measures and, with pure platinum, for the thermo-couples of pyrometers. An alloy containing 10 p.c. of iridium was employed by Mr. George Matthney in the standard measures of length for the International Standards Committee. He afterwards recommended a 15 p.c. alloy for that purpose, and a 20 p.c. alloy as the best for standard weights. Both show extremely high values for elasticity, malleability and ductility, and their uses are merely limited by their cost.

Although all the compounds which platinum forms with the non-metals are decomposed by heat and commonly also by reducing agents, this metal probably forms a larger and more interesting series of salts than any other of the noble metals, its double salts with the alkalis and alkaline earths being especially interesting.

G. T. H.

#### PLATINUM COMPOUNDS.

**Oxygen compounds.** Platinum monoxide  $\text{PtO}$ , which gives rise to the platinum salts, is formed as a grey powder when the hydroxide is ignited carefully; or as a violet powder by igniting calcium platinate and treating the residue with nitric acid. When heated strongly it yields the metal, and when reduced with formic acid it gives platinum black. It forms a stronger oxidising agent than the dioxide, and a better reducing agent than platinum (Wöhler, *Zeitsch. anorg. Chem.* 1904, 40, 423).

**Platinous hydroxide**  $\text{Pt(OH)}_2$  may be formed by the action of caustic soda or potash on the dichloride, or, better, on aqueous potassium platinochloride. It is an oxidising agent and acts as a weak base, some of the salts of which have been prepared.

**Platinum dioxide**  $\text{PtO}_2$  is a black powder obtained by heating the corresponding hydroxide.

**Platinic acid**  $\text{Pt(OH)}_6$  or  $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Pt(OH)}_6$  (Att. R. Accad. Lincei, 1903, 1904, 1905, 35, [iii.] 554; Blondel, *Ann. Chim. Phys.* 1905, [viii.] 6, 81), is prepared by boiling a solution of platonic chloride with caustic potash and treating the basic salt thus formed with acetic acid. When freshly prepared it is almost white, and is readily soluble in acids and alkalis, two of its hydrogen atoms being acidic and two basic. When dried, or on standing, it becomes yellow, and is no longer soluble in dilute acids. Platinic acid forms crystalline platينات of the type  $\text{M}_2\text{Pt(OH)}_6$ , and also of a more complex constitution (Blondel, *L.c.*; Bellucci and Parravano, *Atti. R. Accad. Lincei*, 1905, [v.] 14, [i.] 459; Gibbs, *Ber.* 1877, 10, 1384; Herschel, *Phil. Mag.* 1832, [ii.] 1, 58).

The oxides  $\text{Pt}_2\text{O}_3$ ,  $\text{Pt}_3\text{O}_5$  have been described (Jørgensen, *J. pr. Chem.* 1877, [ii.] 16, 344; Dudley, *J. Amer. Chem. Soc.* 1902, 28, 59), but

it is doubtful whether they really exist (Wöhler, *l.c.*). The *hydrated platinum sesquioxide*,  $\text{Pt}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ,

intermediate between the two foregoing hydroxides, has been prepared by Wöhler and Martin (*Ber.* 1909, 42, 3958).

**Platinum trioxide**  $\text{PtO}_3$  is formed when the hydrated dioxide is electrolysed in a 2N solution of potash at 0°. A brilliant golden-yellow substance of composition  $3\text{PtO}_3 \cdot \text{H}_2\text{O}$  separates at the anode, and the trioxide can be isolated by extraction with very weak acids. It is a substance which loses oxygen readily, but is scarcely attacked by dilute mineral acids. Most reducing agents reduce it to platinum black. It liberates iodine from potassium iodide, but has little effect on alcohol, acetic acid, or many oxidisable organic substances. Many of the hitherto observed reactions of platinum are said to be due to the formation of this oxide (Wöhler and Martin, *Ber.* 1909, 42, 3326; see also Grube, *Zeitsch. Elektrochem.* 1910, 16, 621).

**Halogen compounds.** **Platinum dichloride** or **platinous chloride**  $\text{PtCl}_2$  is formed by heating platinochloric acid  $\text{H}_2\text{PtCl}_4$  to 300°, or by heating spongy platinum in a current of dry chlorine at 240°–250° (Schützenberger, *Ann. Chim. Phys.* 1870, [iv.] 21, 351). It is a greenish-grey insoluble powder, sp.gr. 5.8, which readily decomposes on heating into its elements (Shenstone, *Chem. Soc. Trans.* 1892, 450).

It readily combines with phosphorus trichloride, forming the compounds  $\text{PtCl}_2 \cdot \text{PCl}_3$ ,  $\text{PtCl}_2 \cdot (\text{PCl}_3)_2$ , the aqueous solution of which when evaporated *in vacuo*, form *chloroplatinic phosphorous acid*  $\text{PtCl}_2 \cdot \text{P(OH)}_3$  and *chloroplatinic diphosphorous acid*  $\text{PtCl}_2 \cdot 2\text{P(OH)}_3$  respectively. The latter is decomposed at 12°, forming the white crystalline compound  $\text{PtCl}_2 \cdot \text{P(OH)}_3$ , which at 150° is converted into a yellow powder  $\text{PtClO}_2 \cdot \text{P(OH)}_3$  (Schützenberger, *Bull. Soc. chim.* 1872, [ii.] 17, 428; *ibid.* 18, 153; Rosenheim and Löwenstamm, *Zeitsch. anorg. Chem.* 1903, 37, 394).

Platinous chloride combines with carbon monoxide, forming a number of carbonyl platinochlorides (Pilling, *Chem. Soc. Trans.* 1891, 955).

Platinous chloride dissolves in hydrochloric acid, yielding platinochloric acid or chloroplatinous acid  $\text{H}_2\text{PtCl}_4$ , the potassium, other salts and compounds of which have been prepared (Thomsen, *J. pr. Chem.* 1877, [ii.] 15, 294; Nilson, *ibid.* 260; Magnus, *Pogg. Ann.* 1828, 14, 241; Klason, *Ber.* 1904, 37, 1360; Kurnakoff, *J. Russ. Phys. Chem. Soc.* 25, 565; Pigeon, *Compt. rend.* 1895, 120, 681).

**Platinum tetrachloride** or **platinic chloride**  $\text{PtCl}_4$  is formed when platinum is heated in a current of chlorine (Troost and Hautefeuille, *Compt. rend.* 1887, 84, 916; Hodgkinson and Lowndes, *Nature*, May 3, 1888), or when dry platinochloric acid is heated in a current of chlorine or of hydrochloric acid (Pigeon, *Compt. rend.* 1890, 110, 77; *ibid.* 1891, 112, 1218; *Ann. Chim. Phys.* 1894, [vii.] 2, 433; Pilling, *L.c.*). Hydrates containing 1, 4, 5, and 7 molecules of water have been prepared. In aqueous solution, the tetrachloride behaves as a weak dibasic acid  $\text{H}_2\text{PtCl}_4(\text{OH})_2$ , and salts of

this acid have been obtained (Miolati, *Zeitsch. anorg. Chem.* 1900, 22, 445; also Kohlrausch, *Zeitsch. physikal. Chem.* 1900, 33, 257; Hittorf and Salkowski, *ibid.* 1899, 28, 546; Dittenberger and Dietz, *Ann. Chim. Phys.* 1899, [ii.] 68, 853).

**Platinum trichloride**  $\text{PtCl}_3$  has been obtained by Wöhler and Martin (*l.c.*) by heating platonic chloride in pure dry chlorine at  $390^\circ$  for 10 hours. It forms a dark green nearly black powder, soluble in boiling water, and decomposed by hot concentrated hydrochloric acid into the di- and tetra-chlorides.

A **platinum monochloride**  $\text{PtCl}$  has also been obtained (Sonstadt, *Chem. Soc. Proc.* 1898, 25, 179).

**Platinichloric acid or chloroplatinic acid**  $\text{H}_2\text{PtCl}_6$  is prepared by dissolving platinum in *aqua regia* and removing the hydrochloric acid until all the chlorine is removed. It may also be obtained by passing chlorine through concentrated hydrochloric acid containing platinum black in suspension; or by the electrolysis of platinum black (Weber, *J. Amer. Chem. Soc.* 1908, 30, 29; see also Matignon, *Compt. rend.* 1902, 134, 1497).

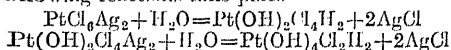
It crystallises with 6 molecules of water and forms reddish-brown deliquescent prisms. It readily yields crystalline salts of the type  $\text{M}'_2\text{PtCl}_6$ , known as the *platinichlorides* or *chloroplatinates* of which the alkali salts are the most important in chemistry. It also forms salts with many organic compounds.

A number of chloroplatinic acids and their salts intermediate between platonic acid  $\text{H}_2[\text{Pt}(\text{OH})_6]$  and the hexachloro acid have been described (Bellucci and Miolati, *Atti. R. Accad. Lincei*, 1900, [v.] 9, ii. 51; *ibid.* 1902, [v.] 11, ii. 241, 271).

Platinous and platonic bromides and the corresponding acids (Meyer and Zühlín, *Ber. 1880*, 13, 101; Halberstadt, *ibid.* 1884, 17, 2962; Bellucci, *Atti. R. Accad. Lincei*, 1900, v. 9, ii. 51), also the iodides and iodic acids (Bellucci, *ibid.* 11, i. 8; Pigeon, *l.c.*; Peterson, *Zeitsch. anorg. Chem.* 1898, 19, 59), the di-fluoride (Moissan, *Compt. rend.* 1889, 109, 807), and mixed halogen derivatives (Hertz, *Ber.* 1896, 29, 411) have also been prepared.

**Nitrogen compounds.** A number of metallic *platino nitriles* or *nitrito platinites* and their oxalo- and other derivatives have been described (Lang, *J. pr. Chem.* 1861, 83, 415; Blomstrand, *ibid.* 1871, [ii.] 3, 207; Nilson, *Ber.* 1876, 9, 1722; *ibid.* 1877, 10, 934; Vézès, *Compt. rend.* 1891, 112, 616; *ibid.* 113, 696; *ibid.* 1897, 125, 525; *Bull. Soc. chim.* 1901, [iii.] 25, 157; *ibid.* 1902, [iii.] 27, 930; *ibid.* 1903, [iii.] 29, 83; Berg, *Zeitsch. anorg. Chem.* 1897, 15, 278).

**Fulminating platinum**  $(\text{OH})_2\text{PtNH}_3\text{Pt}(\text{OH})_2$  strongly resembles ferric hydroxide in appearance. It is prepared by treating hexachloroplatinic acid with silver nitrate in the cold. The silver hexachloroplatinate so formed is decomposed with hot water, and the resulting tetrachloroplatinic acid again treated with silver nitrate, and the new silver salt decomposed by boiling with water for some hours. The following reactions take place—



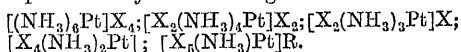
The solution of the dichloroplatinic acid treated with ammonia yields fulminating platinum, which when heated darkens, then detonates violently. A similar compound is obtained if pyridine is substituted for ammonia (Jacobsen, *Compt. rend.* 1909, 149, 574).

The various platinum salts form complex compounds with ammonia, similar in constitution to that of the chromium bases, and existing in two series in one of which the platinum is divalent, in the other tetravalent.

The chief types of platinous compounds are—

The platodiammines  $[(\text{NH}_3)_4\text{Pt}]X_2$ ; platomonodiammines  $[\text{X}(\text{NH}_3)_3\text{Pt}]X$ ; platosamine and platosemidiammine  $[\text{X}_2(\text{NH}_3)_2\text{Pt}]$ ; and platosemiammine  $[\text{X}_3(\text{NH}_3)\text{Pt}]R$ .  $X$  and  $R$  = monovalent acid and basic radicals respectively.

The chief types of platonic compounds are represented by the following formulæ:—



**Magnus' green salt**  $\text{Pt}(\text{NH}_3)_4\cdot\text{PtCl}_6$ , which was obtained by Magnus in 1828 (Pogg. *Ann.* 14, 204) by the action of ammonia on platinous chloride, is the starting-point for the preparation of all these derivatives. When boiled with ammonia it passes into *platodiammine chloride* or *tetrammine-platinous chloride*  $[(\text{NH}_3)_4\text{Pt}]X_2$ . The green salt may also be obtained by the action of potassium platinous chloride on platodiammine chloride, but if the solution is very dilute and neutral, or slightly ammoniacal, and traces of potassium platinichloride are absent, a rose-red crystalline salt is formed, which, when boiled with water passes into the green salt (Jørgensen and Sørensen, *Zeitsch. anorg. Chem.* 1906, 48, 441).

**Literature.**—Gras, *Ann. Chim. Phys.* [ii.] 69, 204; Peyronne, *ibid.* 1844, iii. 12, 193; 1846, [iii.] 16, 462; Reiset, *ibid.* 1844, [iii.] 11, 417; *Compt. rend.* 1844, 18, 1103; Schou, *Zeitsch. anorg. Chem.* 1896, 13, 36; Karnakoff, *ibid.* 1898, 17, 207; Klason and Wauselin, *J. pr. Chem.* 1903, [ii.] 67, 41; Euler, *ibid.* 1904, 37, 2391; Tarugi, *Gazz. chim. ital.* 1900, 30, i. 364; Ray and Shosh, *Zeitsch. anorg. Chem.* 1909, 64, 184; Werner, *Ber.* 1907, 40, 4093; Jørgensen and Sørensen, *l.c.*; and many others). Organic derivatives of ammonia compounds have been described by Klason (*J. pr. Chem.* 1903, [ii.] 67, 1; Jørgensen, *Zeitsch. anorg. Chem.* 1906, 48, 374).

Platinum compounds have been described by ... 1900, 311, 120), and an explosive *potassium platino-azoisimide* by Curtius and Bissow (*J. pr. Chem.* 1898, [ii.] 58, 261).

**Platinocyanic acid**  $\text{H}_2[\text{Pt}(\text{CN})_4]$  is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen or the barium salt with dilute sulphuric acid (Quadrat, *Annalen*, 1849, 70, 300; Weselsky, *J. pr. Chem.* 1856, 69, 276). When crystallised with 5 molecules of water it forms blue rhombic prisms exhibiting a brilliant blue colour by reflected light; when containing more water the crystals have a yellow-green colour with a golden lustre.

**Platinocyanides** may be prepared by dissolving well-washed freshly-prepared platinum sulphide in a solution of the corresponding cyanide.

The colourless solution is then concentrated. The reaction proceeds thus :

$\text{PtS}_2 + 5\text{KCN} = \text{K}_2\text{Pt}(\text{CN})_4 + \text{K}_2\text{S} + \text{KCNs}$   
(Schartel, Ber. 1896, 29, 204); or they may be prepared by double decomposition from the potassium salt which is formed by heating spongy platinum with potassium ferrocyanide to redness, or by dissolving platinous chloride in potassium cyanide (Knopp, Annalen, 1842, 43, 111). The platinumcyanides are characterised by their reaction with the mercury salts with which they first give a white precipitate, which on addition of more mercury salt turns blue. They become luminous when exposed to Röntgen rays, and are used for making screens for the detection of these rays.

Nearly all platinumcyanides fluoresce to a marked degree, the colour and intensity of fluorescence depending on the character of the basic radicle, the state of hydration, the perfection of the crystalline forms, and in some cases on the mode of preparation. Certain of the platinumcyanides exist in two modifications, having the same crystalline form, but, prepared by different methods, they show a difference in all their optical characteristics. It is remarkable that the same compound may be prepared in different ways, and yet show different optical properties. (See, e.g., *ibid.* 1896, 29, 204; also Jackson, *ibid.* 1896, 57).

Some further literature, Bergsöe, Zeitsch. anorg. Chem. 1899, 19, 318; Brochet and Petit, Compt. rend. 1904, 138, 1095; Reynolds, Proc. Roy. Soc. 1909, 82, A, 380. Dicyanodiamidinium platonic chloride  $(\text{C}_2\text{H}_6\text{N}_4\text{O})_2\text{PtCl}_6$  is described by Grossmann and Schück (Ber. 1910, 43, 674).

For  $\text{PtCl}_2$ , see Buckton, Chem. Soc. Trans. 1900, 2, 588; and Bellucci, Gazz. chim. ital. 1900, 30, ii. 588; Grossmann and Schück, Ber. 1906, 39, 1896.

**Sulphur compounds.** Platinum monosulphide  $\text{PtS}$  forms a green powder or glistening needles, prepared by heating platinum sponge with sulphur in a vacuum glass tube (Debray and Deville, Compt. rend. 1879, 89, 587).

Platinum disulphide  $\text{PtS}_2$  may be obtained pure as a steel-grey powder, soluble in 3 p.c. solution of  $\text{H}_2\text{SO}_4$  at  $90^\circ$  with sulphur temperature, and on warming, while the liquid becomes red, containing colloidal platinum sulphide, which is deposited at  $0^\circ$  (Antony and Lucchesi, Gazz. chim. ital. 1896, 26, i. 211).

Platinic sulphate  $\text{Pt}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  forms large orange leaflets (Stuchlik, Ber. 1904, 38, 2913).

A number of *thio* platinum salts have been prepared (Schneider, Pogg. Ann. 1866, 138, 604; J. pr. Chem. [ii.] 48, 411; Hofmann and Höchstlen, Ber. 1903, 36, 3090). *Tellurides*  $\text{Pt}_2\text{Te}$ ,  $\text{PtTe}_2$ ,  $\text{PtTe}$  (Roessler, Zeitsch. anorg. Chem. 1897, 15, 405), and *selenides*  $\text{PtSe}$ ,  $\text{PtSe}_2$ ,  $\text{PtSe}_3$  (Roessler, *ibid.* 1895, 9, 59; Minozzi, Atti. R. Accad. Lincei, 1909, v. 18, ii. 150) also exist.

A platinum compound analogous to purple of Cassius (*v.* GOLD PURPLE) is obtained by the action of stannous chloride on solutions of platinum salts, when a blood-red solution is formed, which darkens after a time, particularly

on warming, finally becoming black and slightly turbid. When shaken with ether or ethyl acetate the red colour is extracted, and on addition of water, a chocolate-brown precipitate is formed, consisting of platinum, tin, and oxygen in varying proportions. When freshly precipitated it is soluble in hydrochloric acid. It does not diffuse through parchment paper, and may be regarded as an adsorption compound of colloidal platinum and colloidal stannic acid, but the former shows none of the ordinary reactions of colloidal platinum. A similar red solution has been obtained by reducing platonic chloride with an ethereal solution of phosphorus in the presence of gelatin (Wöhler, Verh. deut. Naturforsch. Aerzte, 1907, ii. 105; Wöhler and Spengel, Zeitsch. Chem. Ind. Kolloide, 1910, 7, 243).

**Platinum phosphides**  $\text{PtP}_2$ ,  $\text{Pt}_3\text{P}_2$  (Granger, Compt. rend. 1896, 123, 1284), **platonic pyrophosphate**  $\text{PtP}_2\text{O}_7$  (Barnett, Chem. Soc. Trans. 1895, 513), **arsenides**  $\text{PtAs}_2$  and the **arsenite**  $\text{Pt}_3(\text{AsO}_3)_4$  (Stavenhagen, J. pr. Chem. 1895, [ii.] 51, 1); the **silicides**  $\text{SiPt}$ ,  $\text{SiPt}_2$  (Vignaroux, Compt. rend. 1896, 123, 115; *ibid.* 1907, 145, 376); and also **tungstates** and **molybdates** of platinum (Gibbs, Amer. Chem. J. 1895, 17, 73) have been prepared.

**Organic compounds of platinum.** Alkylcompounds may be prepared by the action of platinum methyl iodide and platinum chloride, a number of these substances and their hydroxide, nitrate, sulphate, chloride, cyanide, and platinumcyanide derivatives have been prepared by Pope and Peachy (Chem. Soc. Trans. 1909, 571).

**Platinous xanthate**  $(\text{OEtCS}_2)_2\text{Pt}$  occurs in flat yellow prisms, m.p.  $129^\circ$ – $130^\circ$ , is insoluble in water, but readily soluble in chloroform.

Other platinum salts of thio-organic acids are described by Ramberg (Zeit. ch. anorg. Chem. 1906, 50, 439).

Complex *platinous pyridinehalides* are described by Jörgensen and Werner, *ibid.* 1896, 12, 46; *ibid.* 1900, 25, 353; Klasan, Ber. 1904, 37, 1349.

**Organic phosphorus platinum halides** by Baerheim and Levy (Zeitsch. anorg. Chem. 1905, 43, 34).

**Platinum alginate** is a brown gelatinous precipitate readily soluble in ammonia, forming a yellow solution (Stanford, J. Soc. Chem. Ind. 1886, 220).

For certain other organic compounds, see Werner, *loc. cit.*; Corsa, Gazz. chim. ital. 22, ii. 620; Hofmann and Rabe, Zeitsch. anorg. Chem. 1897, 14, 293; Prandtl and Hofmann, Ber. 1900, 33, 2981; H. and Bugge, *ibid.* 1908, 41, 312; H. and Narbutt, *ibid.* 1925, 41, and Buchner, *ibid.* 1909, 42, 3392; Tschugaeff and Sokoloff, *ibid.* 55; Ostromislensky and Bergmann, *ibid.* 1910, 43, 2768.

**PLUM, Prunus spp.** Many species and varieties are known. As the average of 33 analyses, König gives for the composition of the fruit—

Water	Protein	Free acid (Malic)	Sugar	Other N. free ext.	Fibre and Ash
78.6	1.0	0.8	8.8	4.0	5.8 0.5

For analyses of Californian grown plum and prunes *v.* Colby (Experim. Stat. Rec. 1893, 4, 918), who found the juice of plums to contain

about 18 p.c. of sugar and 0.5 p.c. free acid (as  $H_2SO_4$ ).

The kernel contains amygdalin and emulsin; it is also rich in a fixed oil. The rind contains a wax melting at  $64^\circ$  (Seifert, Landw. Versuchs. Stat. 1894, 45, 29). Plums require and remove from the soil far larger quantities of nitrogen than are demanded by most other orchard crops, e.g. apples or pears. According to American estimates, an average crop of plums (30,000 lbs. per acre), removes about 127 lbs. of nitrogen, 13 lbs. phosphoric acid, and 51 lbs. of potash per acre from the soil, while for apples and pears (each 20,000 lbs. per acre), the figures are 12 and 12 lbs. of nitrogen, 6 and 10 lbs. phosphoric acid and 16 and 36 lbs. potash respectively.

For effect of manuring upon the yield of plums and damsons v. Dyer and Shrivell (Jour. Roy. Hort. Soc. 1903, 27, part 4). H. I.

**PLUMBAGO** v. GRAPHITE.

**PLUMIERIDE** v. AGONIADA BARK.

**PLUMOSITE** v. FEATHER-ORE.

**PODOPHYLLIC ACID**, **PODOPHYLLO-QUERCETIN**, and **PODOPHYLLOTOXIN** v. *Podophyllum* section art. RESINS.

**PODOPHYLLIC v. RESIN** v. RESINS.

**POLARIMETRY.**

### I. QUALITATIVE.

When a ray of light falls on the surface of an isotropic substance like glass, it is, in general,

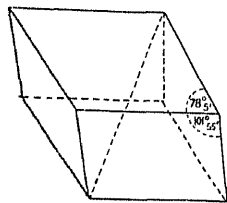


FIG. 1.

bent out of its path at the surface of separation of the two media, according to a law discovered by Snellius in 1621. The incident and refracted rays lie in the same plane with the normal to the surface at the point of incidence, the sine of the angle of incidence

divided by the sine of the angle of refraction being a constant.

In 1609, Bartholinus noticed that if a ray of light enters a crystal of Iceland spar, it splits, usually, into two rays, one of which pursues its way through the crystal according to the ordinary laws of refraction, while the behaviour of the other depends upon the direction of the original beam relative to the crystal face. The fundamental form of Iceland spar is the rhombohedron, Fig. 1, and if the edges of the rhomb be equal, the line joining the obtuse solid angles is the *optical axis*. If the rhomb is not equilateral, the *optical axis* is any line parallel to this direction.

If a mark on white paper be examined through a crystal of Iceland spar, whose refracting face is parallel with the paper, two images will be seen. On turning the crystal about a vertical axis, one of these remains fixed whilst the other moves round it, a line joining the two images being always in the direction of the shorter diagonal of the face of an equal edged crystal. The plane passing through this direction perpendicular to the face of the crystal contains the optic axis and is called the principal plane, the images being termed, respectively, ordinary and extraordinary. A ray incident on a surface cut parallel to the optic axis splits into

two rays, each following the laws of single refraction but with a different refractive index, and when the ray is incident normally to the surface, the two rays coincide in direction but move through the crystal with velocities inversely proportional to their refractive indices,  $\mu_o = 1.654$ ,  $\mu_e = 1.483$ .<sup>1</sup> Generally, however, the extraordinary ray is neither in the same plane with the normal and the incident ray, nor is  $\frac{\sin i}{\sin r} = \text{a constant}$ . If the crystal in the above experiment be tilted at different angles, it will be noticed that the separation of the images varies, and when the light travels through the crystal in the direction of the optic axis there is again no separation, both rays pursue the same path with exactly the same velocity.

The theory of the propagation of these two wave-fronts was developed by Huyghaens, who discovered (1690) that both rays differ markedly from the original beam, for, if passed into another crystal situated similarly to that in which they were produced, they are not further resolved, the ordinary ray passes through as an ordinary, and the extraordinary as an extraordinary ray. If, however, their refracting faces being kept parallel, one crystal be turned through an angle of  $90^\circ$  relative to the other, the ordinary ray from the first passes through the second as an extraordinary and the extraordinary as an ordinary ray. In intermediate positions both rays are divided. Newton suggested that these rays have 'sides' (Optics, 1704, Queries 25, 26), meaning thereby that their properties vary in different directions, but the matter attracted little or no attention until after the lapse of another century, when Malus discovered, in 1808, that light could be brought into this peculiar condition by reflection as well as by refraction (Nouv. Bull. Soc. Philom. 1807-9, 1, 266, 341, 353; 1810-11, 2, 252, 291, 320; Gilbert's Ann. 1812, 40, 119, 132).

If a beam of light fall upon a sheet of glass, an angle of incidence of about  $55^\circ 25'$ <sup>2</sup> giving the maximum effect, part will be reflected and part refracted. Both rays are found to have 'poles,' as Malus put it, and, if allowed to traverse a piece of Iceland spar, whose refracting face is perpendicular to the plane of incidence and whose principal plane is parallel to the plane of incidence, the reflected beam will pass through as an ordinary ray. The refracted ray under these circumstances will pass through as an extraordinary ray. The plane of incidence of the light on the reflecting surface came to be called the *plane of polarisation*.

The theory of the subject is due to Fresnel who, in connection with the phenomena of interference which had been discovered by Young, had just developed the transverse wave theory of light. He explained the difference between the ordinary and the extraordinary rays in Iceland spar by the supposition that, whilst the vibrations of the ether particles causing the ordinary ray take place in one plane only, those causing the extraordinary ray occur in a plane at right angles to the first, and he

<sup>1</sup> The double refraction of Iceland spar is said to be negative. The double refraction of quartz is positive, the indices being  $\mu_o = 1.544$ ,  $\mu_e = 1.553$ .

<sup>2</sup> The angle varies with the index of refraction of the glass.

showed that, on his hypothesis, the vibrations of light reflected from a surface at the polarising angle take place in a plane parallel to the surface and therefore at right angles to what was called the plane of polarisation (Nouv. Bull. Soc. Philom. 1824, 9, 150; Ann. Chim. Phys. 1821, 17, 186).

According to the modern electro-magnetic theory of light as developed by Clerk Maxwell, there is a magnetic disturbance in the plane of polarisation and an electric disturbance perpendicular to it. The latter, therefore, corresponds with Fresnel's vibrations.

In 1811, Arago discovered the phenomenon of the rotation of the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1810-1811, 2, 358, 371, 387; Gilb. Ann. 1812, 40, 145). A ray reflected from a piece of glass at the proper angle was received upon a crystal of Iceland spar. It then splits in general into two rays of unequal intensity and, if the crystal be turned round the direction of the ray as axis, four positions will be found, at right angles, in which

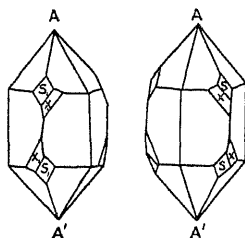


FIG. 2.

only one image appears, alternately ordinary and extraordinary. When the crystal is set in one of these positions, and a piece of quartz, cut perpendicular to the axis  $AA'$  (Fig. 2), is placed in the path of the ray between the polarising mirror and the crystal,

two images appear, complementary in colour—the colours depending on the thickness of the plate—and, if they happen to overlap, the part common to both is white. On turning the crystal the colours change. Something of a similar kind was found for mica and gypsum.

Arago recognised that passage through the quartz plate altered the plane in which the light was polarised, and that the colours were due to the fact that the planes of polarisation of the different rays of which white light is composed, are rotated to different extents. Biot then found (Mém. de l'Institut, 1812, Part I. 218) that the rotation conferred on the plane of polarisation was proportional to the thickness of the plate, and varied with the refrangibility of the light used, the red rays being least rotated and the violet the most, some crystals rotating to the right, others to the left. Later, while engaged on experiments which necessitated the immersion of crystalline plates in liquids to make the polarised rays penetrate the plates very obliquely to the surface, he discovered some of these liquids also to be capable of rotating the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1814-15, 4, 190). This was the case for oil of terebenthine (*l*-pinene, French oil of turpentine) and oil of laurel, each of

plane of polarisation from right to left, whilst oil of citron, and camphor dissolved in alcohol had the opposite effect. Experiments of a somewhat similar character were carried out by Brewster from about 1812, e.g. Phil. Trans. 1815, [i.] 29, and T. J. Seebeck (Schweigger's

Journal, 1813, 7, 259, 382; 1814, 12, 1; Nouv. Bull. Soc. Philom. 1816, 5, 49). Subsequently Biot determined the effect of temperature change on the rotation of oil of terebenthine, examined the influence of solvents, discovered the rotation of cane sugar, applied the polarimetric method to distinguish between natural and artificial camphor and even ascertained that oil of terebenthine in the state of vapour, still retains its rotation<sup>1</sup> (Ann. Chim. Phys. 1818, [ii.] 9, 377; 1819, [ii.] 10, 68).

Fresnel, after discovering circularly polarised light, showed that the rotation of the plane of polarisation of light by quartz cut perpendicular to the axis, could be explained, if on entering the quartz the polarised beam were resolved into two circularly polarised rays travelling through the crystal in the direction of the optic axis, without separation but with different velocities. Then, on emergence, there would be a difference of phase so that the two waves recombine to form again a plane polarised ray whose plane of polarisation is, in general, not that of the original beam. He succeeded in demonstrating the actual existence of these two circularly polarised rays, the principle of his method, if not the actual arrangement of his apparatus, being represented by Fig. 3.  $ABC$  and  $CDE$  are prisms of *l*- and *d*-quartz.

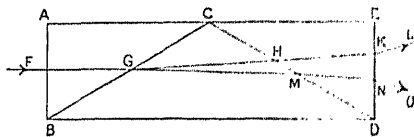


FIG. 3.

so cut that the optic axis of each is parallel to  $BD$ . Now let a ray of plane polarised light<sup>2</sup> fall normally on the surface  $AB$  at  $F$ , and suppose that it splits into two circularly polarised rays which travel in the direction  $FD$ . That whose path is a right-handed helix should travel with a greater velocity in the *l*-prism  $ABC$  and  $CDE$  than in the *d*-prism  $BCD$ . In passing through the system, therefore, this ray should be bent towards the normal at  $G$ , and away from it at  $M$  and also at  $N$ . Similarly, the ray whose path is a left-handed helix should travel more slowly in  $ABC$  and  $CDE$  than in  $BCD$  and be bent away from the normal at  $G$ , towards it at  $H$ , and away from it at  $K$ . The two rays therefore emerge in the directions  $NO$  and  $KL$ . This separation was actually observed, although it was very small, and the two rays were found to be circularly polarised in opposite senses (Ann. Chim. Phys. 1825, 25, 147). Fresnel explained the rotation of liquids in the same way but the experimental demonstration was made much later. The method whose method was similar to Fresnel's, *d*- and *l*-rotatory liquids of the same refractive index being placed alternately in hollow glass prisms (Sitzungsber. Wien. Akad. 1884, 90, ii. 478).

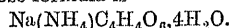
<sup>1</sup> It may be mentioned here that if the ray be though the tube of active substance, and then on the plane of polarisation is annulled during the second, and is polarised in the original plane.

<sup>2</sup> Ordinary light gives the same result.

Although Biot had found that some quartz crystals are dextro- and others laevo-rotatory, he was unable to suggest any property of the quartz—instancing crystalline form—which could be correlated with the phenomenon of rotation, but Herschel (*Trans. Camb. Phil. Soc.* 1821, 1 [i.] 43), remarking that the experiments of Biot gave the impression 'of a want of symmetry in the disposition within the molecules themselves, of some of the elementary forces by which they act on light' (p. 43), pointed out that an indication of this want of symmetry had already been discovered by Haüy in the plagioclism or hemihedrism which shows itself in quartz by the presence of the little facets marked x and x' in Fig. 2, which in some crystals lean towards the right and in others towards the left. Plates cut from a crystal showing facets leaning towards the left, all rotated the plane of polarisation 'to the left, to an observer looking in the direction of the ray's progressive motion, or to the right of one receiving the ray in his eye' (p. 48). At the present time it is conventional to define the sign of rotation in the latter way so that his specimen was what is now called dextro-rotatory. In every other crystal examined the rotation was in the sense that would be expected from the position of the facets.

Some twenty years later, this discovery had a most important influence on Louis Pasteur, who, in 1841, repeated, for practice in crystallography, a research published by de la Provostaye (*Ann. Chim. Phys.* 1841, [iii.] 3, 129) on the crystal forms of tartaric acid, paratartaric acid (racemic acid), and their salts, in regard to which it had been observed by Biot that tartaric acid is optically active (*Mém. de l'Acad.* 1835, 13, 46) whilst racemic acid is inactive (*Ann. Chim. Phys.* 1838, [ii.] 69, 22). In this work (*ibid.* 1848, [iii.] 24, 442) he noticed something overlooked by de la Provostaye, namely that all the tartrate crystals had hemihedral facets, although they were not always very distinct, whereas racemic acid and such of its salts as he examined showed no hemihedrism. He also observed that the ratio of two of the axes in the tartrates is nearly the same, whilst the third differs considerably, and, if crystals of different tartrates be similarly situated, the arrangement of the hemihedral facets is always in the same sense. It then occurred to him that the relationship which had been inferred by Herschel for quartz might also apply in the case of the tartrates. Just about this time, Mitscherlich stated that: 'Sodium ammonium tartrate and sodium ammonium racemate have the same chemical constitution, the same crystal form with the same angles, the same specific gravity, and the same double refraction, in consequence of which their optic axes are inclined at the same angle; . . . the nature and number of the atoms, their arrangement and their distance from each other are the same in both compounds,' and yet tartaric acid in solution rotates the plane of polarisation of light whilst dissolved racemic acid is indifferent (*Monatsber. der Berl. Akad.* 1842; *Compt. rend.* 1844, 19,

720). Pasteur, thinking it possible that Mitscherlich, like de la Provostaye, had overlooked the presence of . . . which might be expected on the tartrate but not on the racemate, then investigated these salts, which were not among those he had already examined. As he expected, the tartrate was indeed hemihedral, but, to his surprise, the racemate was hemihedral also. On closer examination, however, he noticed that whereas the facets on the tartrate crystals all occurred in the same position, in the racemate they appeared, sometimes towards the right, sometimes towards the left. Doubtless still guided by Herschel's idea, he picked out from the mass some of each kind of crystal and when dissolved separately in water one sort gave a dextro-rotatory and the other a laevo-rotatory solution. Fig. 4 shows the appearance of these crystals whose formula is



Racemic acid thus appeared as a compound or a mixture of a peculiar kind perhaps, of

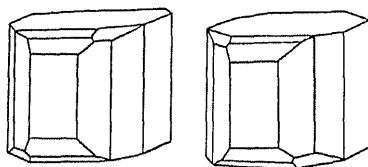


FIG. 4.

ordinary tartaric acid with another variety of tartaric acid, similar in every respect except its rotation and the shape of its crystals which were exactly equal although opposite in sense. Racemic acid, however, does not separate, under any conditions at present known, into the two different forms, and indeed it is only by crystallising it within narrow limits of temperature that sodium ammonium tartrate will separate from solution in the two different forms. Herschel had already a distinct idea of a relationship between asymmetrical crystal structure and optical rotation and the idea was much developed by Pasteur as regards the chemical molecule. He pointed out that many of the objects with which we are acquainted can be separated into two classes: those which are superposable on their mirror images and those that are not. Thus the human body as a whole and apart from minor irregularities, a straight stair, a regular tetrahedron, are identical with their mirror images. But the mirror image of a right hand or of a left hand, of a spiral stair, of an irregular tetrahedron, although each is similar to its object, is not superposable on it; cannot, in the language of Euclid, be similarly situated; the image of a right hand is a left hand. The molecules of the two forms of tartaric acid Pasteur supposed to differ in the same way; the image of a dextro-rotatory molecule is a laevo-rotatory molecule. They would not then be expected to vary in regard to symmetrical forces or properties; they would have the same solubility, the same density, the same amount of water of crystallisation—or lack of it—the same melting-point, the same strength, and in many of their reactions they would behave alike, with ethyl alcohol or sodium hydroxide, for example. But

<sup>1</sup> The figure given by Herschel is incorrect. It represents a twin which, presumably, would have no rotation.

with respect to certain other forces, presumably unsymmetrical, they behave exactly in opposite senses—whilst one rotates the plane of polarisation of light in one direction, the other rotates it in the opposite direction.

Pasteur further found that in each of a pair of enantiomorphous molecules with one chiral centre, figures should be obtained which would no longer be enantiomorphous. Thus, for instance, a right-handed and a left-handed spiral of equal dimensions be each combined with a spiral of different diameter, the two combinations would not be enantiomorphous. Such as they may be supposed to represent, need not be expected to show an identical behaviour even towards symmetrical forces. They might not have the same melting-point, for instance, or the same solubility. This Pasteur found to be the case. He prepared cinchonidine hydrogen racemate and on allowing the solution to evaporate, the acid salt of cinchonidine with levo-tartaric acid separated first, afterwards the corresponding salt of cinchonidine with dextro-tartaric acid also crystallised out. The two were quite different in appearance, in solubility, in melting-point, and from them the two enantiomorphs were obtained. Thus Pasteur introduced that method which, since his time, has been used more than any other for the resolution of substances similar in character to racemic acid.

Pasteur carried his investigation a step further. It was known that commercial calcium tartrate occasionally fermented, with the formation of various products. He imitated this fermentation, first with ammonium tartrate, which was destroyed, and then with ammonium racemate. In the latter case, the liquid, originally inactive, gradually became levorotatory, and from it could be obtained ultimately levo-tartaric acid. The micro-organisms had destroyed the dextro-acid, leaving the levo-acid.

Here, again, Pasteur established another method of a general character for the resolution of substances of the type of racemic acid. (For a fuller account of these researches see *Alcibiades Club*, Vol. 14, W. F. Clay, Edinburgh; also *Proceedings of the Royal Society of Edinburgh*, 1897, 71, 683).

Even this brilliant work, however, supplied no criterion to decide which chemical compounds were similar in character to racemic acid, and might therefore be expected to yield dextro- and levo- isomerides, while theoretical organic chemistry was not at that time sufficiently developed to render possible a correlation of rotatory power with the constitution of naturally occurring active substances. Some twenty years had to elapse before this became possible, the work of Pasteur being the incentive to one attempt to overcome the difficulty, the investigations of Wislicenus on the various forms of lactic acid and the speculations of Kekulé having much to do with another.

As Wislicenus pointed out, the plane formulae in use about 1870 were insufficient to explain the existence of the three known lactic acids, and he suggested that this subtle isomerism might perhaps be represented by different

spatial arrangement of the atoms of the molecules. Paralactic acid and fermentation lactic acid were probably only geometric isomerides (Ber. 1869, 2, 550, 620; Annalen, 1873, 67, 343).

In 1874, van 't Hoff (in a pamphlet) and Le Be (Bull. Soc. chim. 1874, [ii.] 22, 337) published practically identical views, referring the asymmetry which Pasteur had attributed to the molecule of an active compound as a whole to one or more of its carbon atoms. If a carbon atom be combined with four different atoms or groups, and it be assumed that the affinities of the carbon atom are directed towards the angles of a tetrahedron, it is possible to arrange the four groups in two different ways such that the mirror image of the one arrangement is identical with the other arrangement (Fig. 5). Further, such compounds as were known to be optically

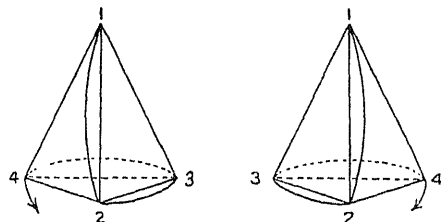


FIG. 5.

active, contained carbon atoms of the above character, whence it might be inferred that any inactive compound containing an asymmetric carbon atom should be capable of resolution into active isomerides.

This idea explained all that Pasteur had discovered about tartaric acid. The constitutional formulae then coming into use, exhibited the presence of two asymmetric carbon atoms in the substance, and by combining two such atoms in different ways it was possible to account for all the existing isomerides. Thus, in Fig. 6, the grouping of the radicles about the upper carbon atom is the same as that about the lower one, and since both the radicles of which the molecule is composed are the same in configuration, the molecule should be active, say in a *dextro* sense. Fig. 7 shows a molecule composed of two radicles each of opposite asymmetry to those of Fig. 6, and should therefore represent *levo*-tartaric acid. A mixture of equal numbers of these molecules will constitute racemic acid, which is capable of resolution into the two active forms, whilst, if two radicles of opposite asymmetry be combined, as in Fig. 8, the molecule obtained should be inactive, because the two parts of which it is composed tend to turn the plane of polarisation of light equally in opposite directions, and, at the same time, it should not be capable of resolution since all the molecules composing it are exactly the same. This is the *meso*-tartaric acid of Pasteur. The spirals drawn round the asymmetric atoms and passing through the groups always in the same sequence, help to show that the twist given to the plane of polarisation of light is in the same sense whichever end of the molecule the ray enters at. The lower formulae of the Figs. 6, 7, 8, show the conventional method of projecting these three dimensional figures on to the plane of the paper.

The work carried out on optical activity since the publication of the views of van 't Hoff and Le Bel has been, for the most part, a splendid

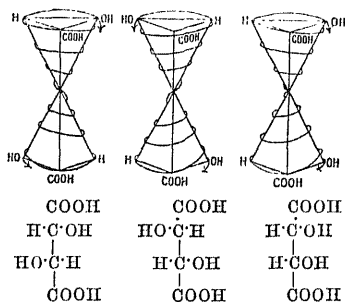


FIG. 6. FIG. 7. FIG. 8.

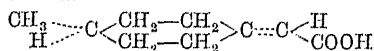
confirmation of them, but, in some directions, there have been developments. It has been shown that carbon is not the only element that can give rise to optical activity. In the case of nitrogen, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1127) were successful in resolving

l-methyl-2-nitro-3-phenyl-2-propylamine hydrochloride by resolution with sodium nitrite (see also Pope and Peachey, *ibid.* 1900, 77, 1072).

Following their activity to the presence of an asymmetric tin atom were obtained by Pope and Peachey (Chem. Soc. Proc. 1900, 16, 12), others containing asymmetric sulphur by Pope and Peachey (Chem. Soc. Trans. 1900, 77, 1072), and Smiles (*ibid.* 1900, 77, 1174), asymmetric selenium by Pope and Neville (*ibid.* 1902, 81, 1552), asymmetric silicon by Kipping (*ibid.* 1907, 91, 209; 1908, 93, 2090), asymmetric phosphorus by Meisenheimer and Lichtenstadt (Ber. 1911, 44, 356), and Kipping and Challenger (Chem. Soc. Trans. 1911, 99, 626), and even asymmetric cobalt (Ber. 1911, 44, 1887) and chromium (*ibid.* 1912, 45, 865) by Werner.

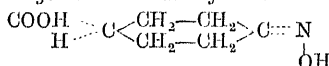
Pasteur attributed the rotation of chemical compounds to the asymmetry of the molecule as a whole and van 't Hoff pointed out, in 1877 (The Asymmetry of Atoms in Space, 1898, 103), that the formula  $\begin{smallmatrix} a \\ \diagup \\ C \\ \diagdown \\ b \end{smallmatrix} \begin{smallmatrix} c \\ \diagup \\ C \\ \diagdown \\ d \end{smallmatrix}$  ought to exist in

two enantiomorphic and therefore, active forms, because if  $a$ ,  $b$ , and the bonds joining them to their carbon atom lie in the plane of the paper,  $c$ ,  $d$ , and their bonds must lie in a plane perpendicular to the first, so that a tetrahedron could be laid through the points,  $a$ ,  $b$ ,  $c$ ,  $d$ . Thus optical activity might exist in a compound containing no asymmetric carbon atom as defined by van 't Hoff. Attempts to prepare such substances failed until Perkin and Pope succeeded in synthesising *l*-methylcyclo-hexyldiene-4-acetic acid



(which is not exactly of the above type) and this was later resolved into its two components by crystallisation of the brucine salt from dilute alcohol (Perkin, Pope and Wallach, Chem. Soc.

Trans. 1909, 95, 1789; see also Perkin and Pope, *ibid.* 1911, 99, 1510). A compound the asymmetry of which is of the same kind is 4-oximinocyclo-hexanecarboxylic acid



(Mills and Bain, Chem. Soc. Trans. 1910, 97, 1866), but the claim that these compounds really contain no asymmetric carbon atom has been disputed by News, 1909, 100, 295; Chem. Soc. Proc. 1911, 27, 285, and Marsh (*ibid.* 1911, 27, 317; see also P. F. Frankland, Chem. Soc. Trans. 1912, 101, 655).

#### Additional Methods for producing Optically Active Compounds.

To Pasteur's three methods for obtaining optically active compounds there may be added some others. Marekwald and McKenzie found (Ber. 1899, 32, 2130) that when mandelic acid was heated with menthol for an hour at 155°, the mandelic acid which remained unacted on, contained a greater proportion of the *l*-form than of the *d*-form, and on this fact a method can be based for separating them.

Again, when an inactive substance, whilst in combination with an active compound, is submitted to some reaction which produces in it an asymmetric carbon atom, it often happens that one arrangement of the groups around this new asymmetric atom is produced in preference to the other. The new asymmetric molecule can then be separated from the one originally active. Thus, for example, by reduction of *l*-menthyl pyruvate  $\text{CH}_3-\text{CO}-\text{CO}-\text{OC}_{10}\text{H}_{19}$ , *l*-menthyl lactate  $\text{CH}_3-\text{CH}(\text{OH})-\text{CO}-\text{OC}_{10}\text{H}_{19}$  was obtained (McKenzie, Chem. Soc. Trans. 1905, 87, 1373), and the lactic acid separated from this was found to be slightly *l*-rotatory. By such processes of *asymmetric synthesis*, McKenzie has produced other active compounds (*ibid.* 1904, 85, 1249; 1905, 87, 1004; 1906, 89, 365).

An ingenious asymmetric synthesis was also carried out by Marekwald, by heating the acid brucine salt of *l*-valeric acid, when valeric acid was obtained containing a slight excess of the *l*-isomer (Ber. 1904, 37, 4696). These methods are, however, meanwhile only of theoretical interest.

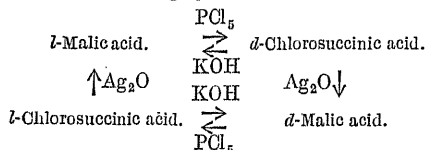
The 'Walden Inversion.' Pasteur showed that *d*-tartaric acid can be converted into *l*-tartaric acid by an indirect process. By heating *d*-tartaric acid under certain circumstances (Pasteur, Compt. rend. 1853, 37, 162; Jungfleisch, Bull. Soc. chim. 1872, 18, 201; Winther, Zeitsch. physikal. Chem. 1906, 56, 466, 720), a rearrangement of the groups about the asymmetric atoms takes place and ultimately an inactive mixture of racemic acid and mesotartaric acid is obtained. The racemic acid can then be resolved by one or other of the processes he had discovered. It would be possible, theoretically, to transform practically the whole of a given quantity of *d*-tartaric acid into the *l*-form, but the experimental difficulties would be very great. Since the method proceeds by racemisation, the substance operated on passes through a stage of inactivity.



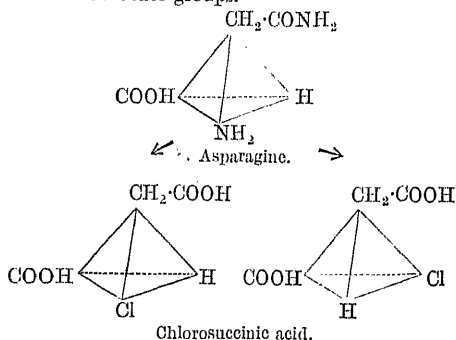
In certain cases, however, it is possible to transform a molecule of one asymmetry into a molecule of opposite asymmetry without passing through any stage of inactivity. *L*-levorotatory asparagine when acted on by nitrous acid yields *l*-levorotatory malic acid, and Walden found that *l*-malic acid yielded with phosphorus pentachloride, a *d*-dextrorotatory chlorosuccinic acid, which therefore

Tilden (Ber. 1895, 67, 494), observed that *l*-levorotatory asparagine gave with nitrosyl chloride a *l*-levorotatory chlorosuccinic acid; whilst Walden, about the same time, discovered (Ber. 1895, 28, 2769) that this asparagine treated directly with bromine and nitric oxide gave a *l*-levorotatory bromosuccinic acid. Thus, starting from *l*-levorotatory asparagine, we can prepare according to the reagents used, either *l*-levorotatory or *d*-dextrorotatory chlorosuccinic acid.

Later, Walden (Ber. 1896, 29, 133) completed the following cycle:—



Caustic potash and silver oxide act thus on the chlorosuccinic acids in an exactly opposite manner. One of these changes must be abnormal being accompanied by an exchange of two of the radicles attached to the asymmetric carbon atom. In one case the  $\text{NH}_2$  group of the asparagine is replaced directly; in the other it, or the chlorine atom which is substituted for it, exchanges places at the same time with one of the other groups.



These reactions are generally accompanied by a little, and often by a great deal, of racemisation.

So far, little of a really general character has been discovered about this most interesting reaction. For further details the papers of Walden (Ber. 1899, 32, 1833), Fischer (*ibid.* 1907, 40, 489; 1908, 41, 889, 1286, 2891; Annalen, 1911, 381, 123), and McKenzie (Chem. Soc. Trans. 1908, 93, 811; 1910, 97, 2564, etc.) should be consulted in addition to the Reports, and P. F. Frankland, Chem. Soc. Trans. 1912, 101, 672.

## II. APPARATUS.

The apparatus used by Biot (Ann. Chim. Phys. 1840, [ii.] 74, 428) and others consisted of a polarising mirror, the light from which, after passing through the substance under investigation, was examined by means of a double refracting rhomb of Iceland spar, or a prism such as that of Rochon or Wollaston, adjustment being made to those positions in which one or other of the images vanished.

A great improvement was made by Nicol (Edin. New Phil. Jour. 1828, [ii.] 6, 83; 1831, [ii.] 14, 372; 1839, [ii.] 27, 332), who invented the prism bearing his name (Fig. 9). It is usually made from a rhomb of Iceland spar about three times as long as broad, and the end

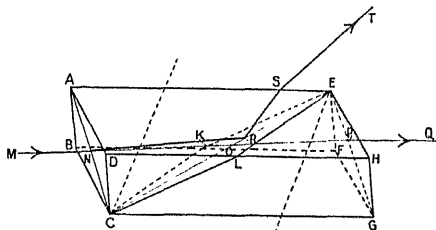


FIG. 9.

faces, ABCD and EFGH should first be ground down so as to reduce the acute angles EAC and CGE from  $71^\circ$  to  $68^\circ$ , but this seems seldom to be done (S. P. Thompson, Phil. Mag. 1886, [v.] 21, 479). The prism is then cut through in the plane ECKL perpendicular to the principal section, in the plane through ACGE. The plane ECKL makes an angle of  $90^\circ$  with the faces ABCD and EFGH. The two halves of the prism are then cemented together again in their original position by means of Canada balsam or Copaiva balsam, the indices of refraction of which lie between those for the ordinary and the extraordinary rays. The index of refraction of the ordinary ray being 1.654 and that of Canada balsam 1.55, it can easily be shown that any ray whose angle of incidence is greater than  $69.5^\circ$ , will be reflected out of the prism. On looking through the prism and tilting it so as to allow the rays to fall very obliquely on the face ABCD, this limit is marked by a series of interference spectra.

The other limit is conditioned by the fact that whereas the index of refraction of the ordinary ray, 1.654, applies in any direction through the crystal, that for the extraordinary ray, 1.483, only applies to the optic axis. As the angle of incidence through the crystal approaches more nearly to that of the optic axis, the value of  $\mu$ , approaches 1.654, and in some intermediate position will have the value 1.55, equal to that of the Canada balsam. All extraordinary rays having a value greater than this are liable, like the ordinary rays, to be totally

It should be noted that the direction of the plane of section is practically immaterial; all that is necessary is that it should make a suitable angle with the prism. If the plane were laid from the vibrations of which are plane, would be reflected out to the prism, whilst the extraordinary ray would be reflected before.

reflected at the balsam film. Fig. 10 shows the prism in section through  $ACGE$ . All rays below  $wv$ —such that the angle  $vxc$  is about  $10^\circ$ —ordinary or extraordinary, suffer total reflection.

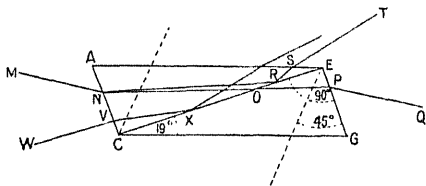


FIG. 10.

On tilting the prism so that the rays fall almost normally on the refracting face, this limit is marked by a broad blue and violet band. All rays, therefore, between  $MN$  and  $wv$  should be polarised in passing through the prism. The angle between these directions is some  $32^\circ$ .

The action of the prism does not depend on the separation of the two rays which occurs in the crystal. It is usually a cone of light that enters the prism so that ordinary and extraordinary rays may travel side by side, but on account of their different velocities in the crystal the former are totally reflected at the film whilst the latter pass through it. The vibrations constituting the ordinary ray are supposed to take place in a plane parallel to  $nd$ , those of the extraordinary ray in one parallel to  $ac$ , and therefore they are polarised in planes at right angles to these.

Fig. 11 represents a Nicol prism, end on. The principal plane passes through  $AC$  perpendicular to the plane of the paper. If a source of light be examined through two Nicols placed one behind the other so that their principal planes coincide (Fig. 12), the vibrations which pass through  $BEFH$ —the remote prism, the

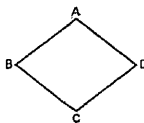


FIG. 11.

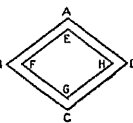


FIG. 12.

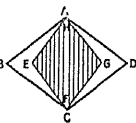


FIG. 13.

polariser—and which are parallel to  $EG$ , will also pass through  $ABCD$ ; but when the prisms are crossed (Fig. 13), the light which passes through  $BEFH$ , vibrating parallel to  $EG$ , is stopped by the analyser,  $ABCD$ , so that part of the field appears dark.

The Nicol prism, however, has several defects, one being the expense of large, clear pieces of spar. For this reason, Foucault (Compt. rend. 1857, 45, 238) invented a prism (Fig. 14) whose length is only about 1.25 times that of one of the sides of the refracting face, the plane of section making with the upper and lower edge an angle of  $59^\circ$ . The Canada balsam is replaced by air. An ordinary ray in the prism incident on this film at any angle greater than  $37^\circ 10'$  will be totally reflected, the field being limited on this side by interference fringes; an extraordinary ray incident on the film at any angle greater than  $42^\circ 20'$  will also be totally reflected, the limiting position being marked by a broad red band. Between these

angles ordinary rays will be totally reflected and extraordinary rays will pass through. The field of view is thus very narrow, only comprising for the rays before they enter the prism, some  $8^\circ$ .

Again (1), part of the light incident on the sloping end face of a Nicol is reflected there,

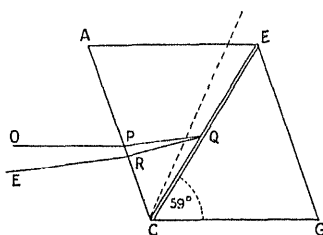


FIG. 14.

and (2) a ray of light falling on the prism in the direction of the axis of length, emerges parallel to its original direction but somewhat displaced, so that if the Nicol is rotated the image circles round the field, this being the case even if the ends of the prism are cut square, as shown in Fig. 15. The extraordinary ray will pass through the prism without displacement only if the

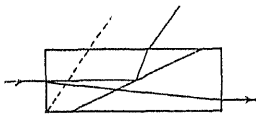


FIG. 15.

refracting surface is cut parallel to the optic axis. A prism, cut as shown in Fig. 16, which partly corrects these faults, was first described by Hartnack and Prazmowski (Ann. Chim. Phys. 1866, [iv.] 7, 181). The end faces are still inclined at an angle to the axis, but the plane of section is perpendicular to the optic axis.

S. P. Thompson (Phil. Mag. 1886, [v.] 21, 478) modifies the Nicol prism so as to improve considerably its polarising properties.  $luzr$  (Fig. 17) represents a section of a rhomb of spar,  $lJ$  being

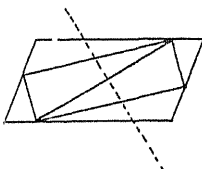


FIG. 16.

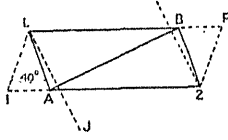


FIG. 17.

the direction of the optic axis. In an ordinary Nicol, the plane of section would pass from  $l$  to  $z$ . The acute solid angles at  $l$  and  $r$  are cut off by the parallel planes  $lA$ ,  $zB$ , such that  $\angle lA = 40^\circ$ ; the plane of section  $AB$  is almost at right angles to  $lA$  and  $zB$ . There is thus comparatively little loss of material, and since the rays travel through the prism nearly perpendicular to the optic axis, the blue band which marks the limit of the transmitted extraordinary waves is thrown back so that with a shorter prism a field of about  $39^\circ$  is obtained.

Other prisms, more or less alike, have been described by S. P. Thompson (Phil. Mag. 1881, [v.] 12, 349), R. T. Glazebrook (*ibid.* 1883, [v.]

15, 352), and P. Glan (Carl. Rep. 1880, 16, ii. 9, 570; Fortschr. d. Physik. 1880, [v.] 10, 247). Fig. 18 gives a rough idea of how this prism is situated relative to the original crystal. By planes perpendicular to the optic axis, the solid

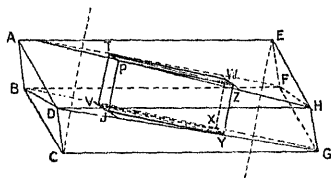


Fig. 18.

angles at C and E are first removed, the prism  $TVJP, WXYZ$ , being then cut out of the remaining spar. The plane of section is laid through  $TVZY$ . The optic axis is thus parallel to the refracting faces,  $TVJP$  and  $WXYZ$ , while the balsam film lies in a principal plane of section, that is, is parallel to the optic axis. There is great waste of material in cutting this prism, but its angle of view is increased and the polarisation is very perfect.

The prism (Fig. 19), described by Lippich (Wien. Sitzungsber. 1885, ii. 91, 1079; Beibl. Ann. d. Phys. 1887, 11, 455) for his polarimeter,

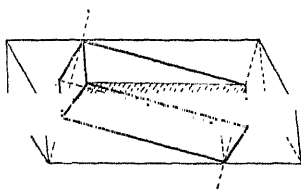


Fig. 19.

has straight end faces of square section and a linseed oil film. The optic axis is perpendicular to the axis of length, but its position relative to the plane of section is immaterial.

Fig. 20 shows the modern form of Nicol prism. A ray of light falling normally on the refracting face does not separate into two rays pursuing distinct paths through the crystal, but at the balsam film the ordinary ray is reflected out whilst the extraordinary ray passes on without deviation. If the optic axis is parallel

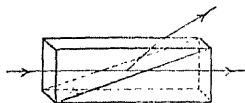


Fig. 20.

to the plane of section the prism is of the Glan-Thompson variety, whilst if it is perpendicular to the plane of section the prism is technically referred to as a Lippich Nicol, although this is not strictly in accordance with Lippich's own statement (*v. supra*). The two parts of the prism are usually cemented together with linseed oil, which is superior to Canada balsam, but takes a long time to dry.

A paper read by E. Sang before the Royal Society of Edinburgh in 1837, discussing the theory of the Nicol prism, is remarkable, partly because fifty-four years elapsed before it was published (Proc. Roy. Soc. Edin. 1891, 81, 323), but also because it contained the first suggestion

for a different type of prism, one to transmit the ordinary and reflect out the extraordinary ray. A right prism of dense glass whose index of refraction is, preferably, just the same as that for the ordinary ray in Iceland spar, is cut through obliquely (Fig. 20 may be taken to illustrate this prism also) and a thin lamina of Iceland spar or sodium nitrate, cut parallel to the optic axis, is introduced between the two parts and brought into optical contact with the cut faces or joined to them by means of some cement with an index of 1.654 or higher. A beam of light passing from the glass to the spar separates into two rays. The ordinary ray, with the same index in the spar as in the glass, goes straight through. For the extraordinary ray, however, the index is much lower in the spar than in the glass and if the ray is incident on the layer of spar at an angle of  $74^\circ$  or more, will not penetrate it at all. This idea was discovered also by Jamin (Compt. rend. 1869, 68, 221; Pogg. Ann. 1869, 137, 174), and a description of a prism on this principle was given by E. Bertrand (Compt. rend. 1884, 99, 538), which, by means of a double plane of section had a field of view of  $98^\circ$ .<sup>1</sup>

*The Polarimeter.* Nicol's prism appears first to have been used in a polarimeter by Mitscherlich (Lehrbuch der Chemie, 4th ed. 1844, i. 361), whose instrument (Fig. 21) was fitted at one end with a Nicol prism beyond which a

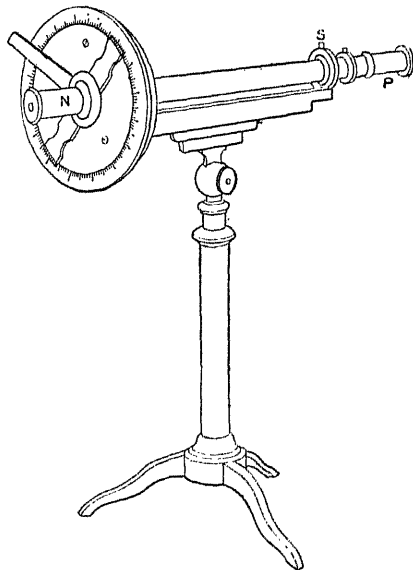


Fig. 21.

source of monochromatic light was placed. At the other end, another Nicol was fixed to a pointer which could be turned round over a graduated scale. The prisms were then set to the position of maximum darkness, which is the zero point of the instrument. If an active substance be interposed between the crossed Nicols the field will become more or less illuminated.

<sup>1</sup> An article "On the Nicol Prism and its Modern Varieties," by S. P. Thompson, containing a bibliography of the subject, will be found in the Proceedings of the Optical Convention, 1905, p. 216.

and in order again to reach the position of maximum darkness the analyser must be turned round either towards the right hand—at the top of the scale, clockwise—or towards the left hand. In the former case, the substance is dextrorotatory, in the latter, levorotatory. Adjustment is always made for the position of maximum darkness, since about this point a small displacement of the prism makes a considerable difference to the eye. The position of maximum brightness is much more difficult, in fact impossible, to adjust to.

Suggestions to obtain greater sensitiveness were made by Robiquet and by Wild, whilst a very ingenious prism was invented by Jellett (Brit. Assoc. Rep. 1860, 29, 13), but perhaps the most commonly adopted proposal was that of Laurent (Journ. de Physique, 1874, iii. 183; Dingt. poly. J. 1877, 223, 608). He placed between the polariser and the analyser, close to the former, a glass plate to which is cemented a half disc of quartz or gypsum cut parallel to the axis, called a half wave length plate. The general arrangement is shown in Fig. 22.  $r$  is the polariser, generally a Foucault prism,  $p$  the glass plate partly covered by the quartz half

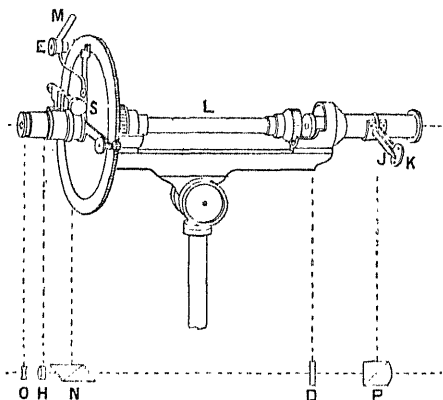


FIG. 22.

disc,  $N$  the analyser, usually a Nicol prism. The telescope  $OH$  is focussed on the straight edge of the quartz plate. In Fig. 23, let the circle  $rgk$  represent the polariser diaphragm;  $rgk$  is the

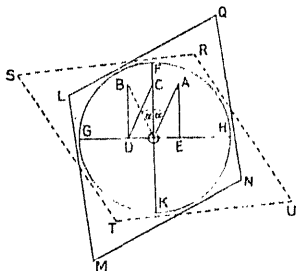


FIG. 23.

half disc of quartz whose optic axis may lie in any direction in the plane of the paper such as  $OB$  or  $DC$  or  $OG$ . Suppose that it is parallel to  $OC$ . The direction of vibration of light waves from

the polariser,  $rstv$ , passing through the diaphragm as seen end on, will be, for example,  $OA$  representing those falling on the glass plate, and  $OC$ , representing those falling on the quartz. The wave  $OA$  on its passage through the glass plate, may be regarded as resolved into two components, vibrating respectively parallel to  $OB$  and to  $OC$ . They travel with the same velocity and the same wave length, the resultant being thus always parallel to  $OA$ . A wave falling on the quartz plate, however, like  $OC$ , is resolved into a component parallel to  $OB$ , the ordinary ray, and one parallel to  $OC$ , the extraordinary ray, these being in reality very narrow ellipses (P. G. Tait, Light, 1889, p. 253; W. Voigt, Ann. d. Physik. 1905, [iv.] 18, 645). At the moment when the light touches the plate the particle of ether at  $D$  of the component  $OB$  is displaced towards  $O$ , and simultaneously the particle of ether at  $D$  of the component  $DB$  is displaced towards  $B$ , the resultant being in the direction  $OC$ . These travel through the plate with different velocities, that of the ordinary ray,  $OB$ , being the greater in the ratio 1.553/1.544. After a certain short interval of time, therefore, the extraordinary ray will have fallen one half wave length behind the ordinary ray. At this moment the vertical displacement is  $OC$  whilst the horizontal displacement is  $OB$ . The resultant is thus  $ON$ , the plane of vibration of the light having been turned through an angle  $2\alpha$  where  $\alpha$  is the angle between the principal plane of the polariser and the optical axis of the quartz plate. As the two components proceed further into the quartz plate, the ordinary ray gains a whole wave length which brings the resultant back into its original position parallel to  $OC$ . In pursuing its way through the quartz plate, the plane of vibration of the light thus oscillates between the directions  $OB$  and  $ON$ . The plate is made of such a thickness that, on emergence, the ordinary ray is one half wave length ahead of the extraordinary ray for the kind of light used, and therefore the plane of vibration is parallel to  $OB$ . Whatever angle the original vibrations may make with  $OB$ , passage through the quartz plate inverts it symmetrically. The special character of this rotation of the plane of vibration of the incident light by the quartz plate should be carefully noticed. It is of an entirely different character from the rotation which would be produced by a plate of quartz cut perpendicular to the axis.<sup>1</sup>

If now the light which has passed through the whole polariser system be examined by a Nicol prism,  $LMNQ$ , placed as shown in the figure, its principal plane at right angles to that of the polariser, the rays that have traversed the glass plate and vibrate parallel to  $AO$  will be stopped by the analyser and the half  $rgk$  of the circular field will appear dark. But those that have come through the quartz plate and are parallel to  $BO$  will pass to a considerable extent through the Nicol so that  $rgk$  will appear relatively bright. If the principal plane,  $LN$ , of the analyser be set perpendicular to  $BO$ ,  $rgk$  will appear dark and  $rgk$  bright. Midway between these positions, the whole field should appear

<sup>1</sup> An instrument dependent on the action of a quartz crystal on the axis, or on a cell containing a liquid suggested by J. H. Poynting (Phil. Mag. 1880, [iv.] 10, 18).

uniformly dark. If the analyser be turned through  $90^\circ$  so that its principal plane is parallel to the axis of the quartz plate the whole field should appear uniformly bright.

The accuracy of a setting depends on the size of the angle  $\alpha$ . If it be small a very slight movement of the analyser should suffice sharply to reverse the relative brightness of the sides of the field. The milled head is then oscillated back and forward from a position of darkness on one side to a position of similar darkness, as judged by the eye, on the other, the oscillations being gradually narrowed down until the median position is reached. The angle  $\alpha$  must not be made too small, however, as then the amount of light cut off is very great and the eye ceases to be able to distinguish clearly between the brightness and darkness of the two halves of the field. The Laurent polarimeter can be used, of course, with only one kind of monochromatic light made for sodium light, passage through a plate of before entering the polarising system.

The Lippich instrument is that most commonly used at the present time (Wien. Sitzungsber. 1885, ii. 91, 1079; 1895, ii. 105, 317). It is accurate, may be used with any kind of monochromatic light, and can be made to give a double or a triple field, the latter being the more delicate. Fig. 24 shows a plan of the arrangement.  $P$  is the polariser, just beyond

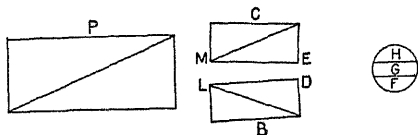


FIG. 24.

which and taking the place of the quartz plate of the Laurent instrument, are two small prisms, each of the same depth but about one half the width of the polariser. For the small prisms both Hilger and Schmidt and Haensch use Lippich Nicols, whilst for the polariser Hilger uses a Lippich and Schmidt and Haensch a Glan-Thompson Nicol. Figs. 25 and 26 represent these systems in perspective, one of the small prisms being

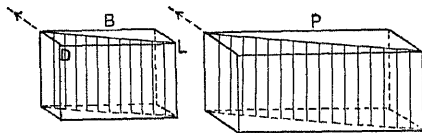


FIG. 25.

omitted in each case. The direction of the optic axis is indicated by the dotted arrows. The polariser is rectangular, but the small prisms have an angle of about  $93^\circ$  at  $D$  and  $E$  and are of about  $87^\circ$  at  $L$  and  $M$  (Fig. 24). The small prisms are fixed so that their faces  $LD$  and  $ME$  are inclined at a slight angle to the axis of the instrument, but the edges  $D$  and  $E$  are parallel or very nearly so. The eyepiece is focussed on these edges, which usually appear

as faint lines dividing the field into three parts. Of these,  $r$  is illuminated by light which has passed through  $P$  and  $B$ ;  $g$  by light which has passed through  $P$  only; and  $h$  by light which has passed through  $P$  and  $C$ . The polariser  $P$  is

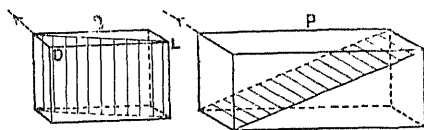


FIG. 26.

capable of rotation some  $15^\circ$  about the axis of the instrument, and in average work is placed so that its principal plane makes an angle of  $4^\circ$  to  $5^\circ$  with the principal planes of the small prisms. If now this system be viewed through the analyser with its principal plane placed perpendicularly to that of  $P$ ,  $g$  should appear dark and  $r$  and  $h$  fairly bright. If the analyser be turned so that its principal plane is perpendicular to those of  $B$  and  $C$ ,  $r$  and  $h$  should appear dark and  $g$  relatively bright. The analyser should then be oscillated about between these positions, the movements becoming smaller and smaller, until the final adjustment is reached.

*Source of light.* The light commonly used for polarimetric purposes is that afforded by incandescent sodium chloride vapour. Fig. 27 represents one lamp suitable for producing it and another is shown in Fig. 28. In the former, salt is placed in a little movable spoon which is then swung into the flame; in the latter, a large

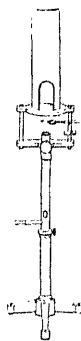


FIG. 27.

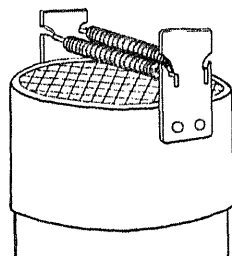


FIG. 28.

size Meker burner is fitted with side pieces, in each of which are slits to receive two fairly stout platinum wires bent at right angles at the ends. Round each wire is rolled a piece of platinum gauze about  $1'' \times 1\frac{1}{2}''$ . Pieces of sodium chloride, which have been fused, are laid on the rolls of gauze after the burner has been lit. The salt melts and sinks into the meshes of the rolls, from which it slowly volatilises. The late Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 617) allowed what was practically an oxy-hydrogen flame to play on the side of a platinum boat containing sodium chloride. Another device has been described by H. E. Armstrong (Proc. Roy. Soc. 1908, A, 81, 113). This may be used instead of the chloride, as it gives a more intense light, but a serious disadvantage lies in the fact that the

bromine vapour given off may injure the polarimeter.

The light from a burner of sodium chloride is not truly monochromatic. There is a slight continuous spectrum, the blue from the Bunsen flame being fairly strong, so the light is usually filtered through a saturated solution of potassium dichromate, which removes the blue and green rays and is sufficient for most purposes. Sometimes a small cell, 1.5 cm. long containing uranic sulphate solution, may be used in addition to the potassium dichromate, as it removes any red rays that may be present; but the best method of purifying the light is by spectral analysis, a direct vision spectroscopic being placed between the eye and the analyser or in front of the polariser. Details of the former method are given in a paper by Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 609).

In a stricter sense, however, sodium light is not monochromatic, for its spectrum consists of two lines very close together,  $D_1$  of  $\lambda=589.62 \mu\mu$  and  $D_2$  of  $\lambda=589.02 \mu\mu$ , so that the light reaching the polariser is a resultant whose optical centre lies between these wave lengths

in proportion to the relative intensity of the lines, which varies with the density of the vapour in the flame and this might have to be taken account of in very accurate work. It is therefore desirable to keep the brightness of the flame as constant as possible whilst a set of readings is being made. Otherwise as the brightness falls off the readings may vary a little.

Monochromatic light may also be obtained from the mercury arc lamp, in the spectrum of which there are four chief lines, one in the blue of  $435.9 \mu\mu$ , two in the yellow of  $579$  and  $576.9 \mu\mu$  respectively, whilst the strongest and most important is that in the yellow-green of  $546.1 \mu\mu$ . The other rays are filtered out by a suitable screen or by some method of spectral purification, and the last line is found very useful for polarimetric purposes (see Lowry, Phil. Mag. 1909, [vi.] 18, 320). If this light be utilised, however, comparative measurements with sodium light should always be given, as otherwise much of the value either of the new data or of the data already amassed for sodium light would be lost.

*The polarimeter.* Fig. 29 shows diagrammatically a modern polarimeter, as made by Schmidt

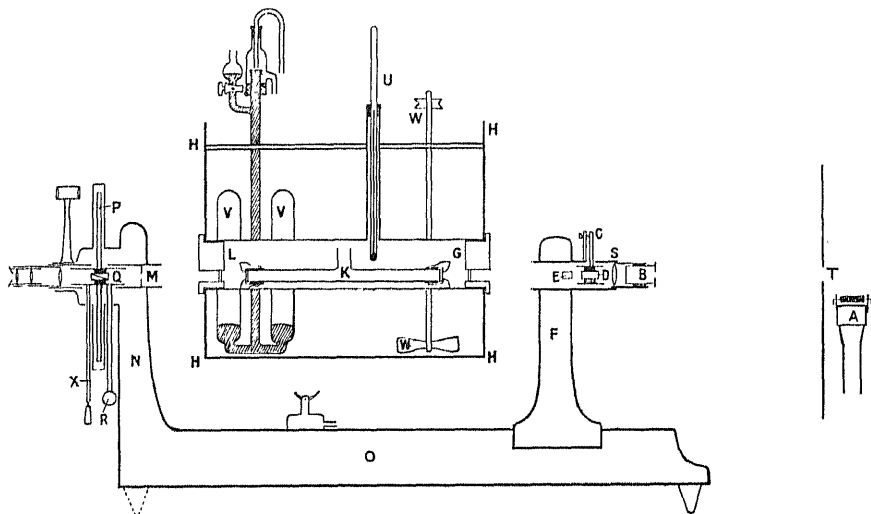


FIG. 29.

and Haensch, Berlin, who, however, supply a different heating apparatus. The lamp A is so placed that a sharp image of the flame, or the Bunsen burner in front of it, is thrown by the lens S on the diaphragm at M. B is a cell containing saturated potassium dichromate solution. By means of C, the angle of incidence can be turned about its axis and thereby the angle altered. The observation tube K lies in a wider tube which passes through a copper bath P containing water or other liquid. This bath is kept at any desired temperature by means of the thermoregulator V (see Ind. 1902, 21, 456) and the stirrer W. A thermometer U indicates the temperature inside the tube LG, which may be taken as identical with

that in the observation tube. LG is closed at L and G by two wooden blocks, the holes in which are closed by small glass discs. Q, the analysing Nicol, is fastened to the graduated circle R, which is enclosed in a cover to protect it from the fumes of the laboratory. The lever X attached to the analyser and the graduated circle, makes the rough adjustment; the fine adjustment is made by means of the screw R. There is also another screw (not shown in the figure) by which the analyser can be turned about its axis independently of the graduated circle to adjust the zero point of the instrument. It may be noticed that when the half shadow—the sensitiveness—is altered by moving the lever C, the zero point is thereby also altered. The sensitiveness ought therefore only to be varied very cautiously and the zero point should be ascertained at intervals, best along with each reading, in an interesting case

in point, see Chem. Soc. Trans. 1905, 87, 618.

The water in the thermostat *HHHH* should be covered with a layer of medium paraffin oil, which, by preventing evaporation, tends to keep the temperature constant. By means of the apparatus shown, the bath can be kept within about  $0.01^\circ$  of a given temperature for several months.

For experiments at temperatures above  $80^\circ$ , a rather small bath filled with oil is best—when the temperature can be raised to  $170^\circ$  or still higher if the joints of the bath are brazed.

Another form of heating apparatus is shown in Fig. 30. *r* is the polariser and *a* the analyser of the instrument. Between these, and having

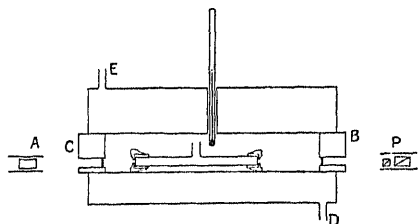


Fig. 30.

the same axis, is supported in some suitable manner, a double cylinder of brass or copper. The observation tube rests in the position shown, and the tubes *r* and *p* allow either of a current of water at some definite temperature being circulated through the cylinder or of steam or other vapour such as that of aniline or nitrobenzene being blown through the apparatus until the temperature has become constant in the observation tube. For an illustration of an instrument fitted in just a slightly different manner, see Scheuer, *Zeitsch. physikal. Chem.* 1910, 72, 569.

**Polarimeter tubes.** Fig. 31 shows the end of a polarimeter tube of the simplest type. Near each end of the glass tube there is fastened a metal collar having a screw cut on it. The ends of the tube are ground parallel and fitted with discs, *A*, of glass, which ought always to

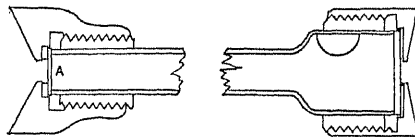


Fig. 31.

Fig. 32.

be carefully examined before use as occasionally they are slightly active on account of internal strain, when they should, of course, be rejected. Metal caps press the glass discs against the ends of the tube, rubber washers equalizing the pressure between them. The caps must not be screwed on too tightly as this may cause the discs to become birefringent and vitiate the readings. In some patterns of tube, a bayonet joint is used instead of a screw so that the pressure on the discs is at least always the same.

In some tubes one end is of the form shown in Fig. 32. Any bubble that has developed owing to contraction on cooling, can easily be

moved into the expanded part of the tube where it does not interfere with the field of view. Especially in small tubes, however, the expanded end greatly increases the capacity of the tube, which is often a serious objection, and tubes of the form shown at *K* in Fig. 29 are much to be preferred, as they readily allow for any contraction or expansion, and can therefore be used for determinations over a moderate range of temperature if care be taken not to melt the sealing wax securing the collars on to which the caps are screwed. Jacketed tubes are also used such that water or other liquid at a desired temperature can be circulated round the tube. This involves the supply of water at constant temperature, which is rather troublesome; a suitable form of apparatus for this is described by Lowry (*Trans. Faraday Soc.* 1907, 3, 119). With many polarimeters, on account of the form of the stand, this is the only method of heating that can be employed. However possible, it is better to use a method like that shown in Fig. 29, which can be adjusted to any required temperature. In sugar factories, for instance, where, especially in the case of invert sugars, it is desirable always to polarise at a definite temperature to avoid the necessity of correcting the readings, a thermostat might be kept at one temperature for, probably, a year at a time without the necessity of renewing any of the parts, and would be found very useful.

Tubes like that shown in Fig. 33, are suitable for investigations over a wide range of temperature. A glass tube with a side piece is fitted,

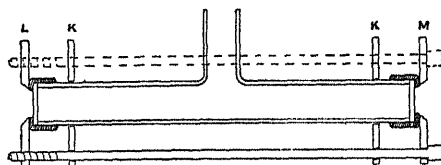


Fig. 33.

somewhat loosely, at each end with a brass ring *K*. The discs are then placed in position and short pieces of rubber tubing drawn over the ends of the tube so as to project beyond the discs, thus serving to prevent leakage and as washers as well. Two other brass rings, *M*, *L*, are placed, one at each end and secured there by brass rods which pass freely through three holes in *M* and *K*, *K*, and screw into holes in *L*. The rings *K*, *K* should be near the ends of the tube, their object being to keep it in position between the rings *M* and *L*. This tube may be used up to a temperature of about  $180^\circ$ , at which the rubber becomes very soft. For slightly different forms, see Chem. Soc. Trans. 1901, 79, 170.

**Determination of density.** Another operation of importance in polarimetric work is the determination of the specific gravity of liquids. This may be done by means of a hydrostatic balance, by hydrometers, by the Westphal balance, by specific gravity bottle, by dilatometer or by pycnometer. The last is probably the most accurate as well as the simplest and is most generally used. For details see article SPECIFIC GRAVITY.

**Methods of expressing rotatory power.** Several expressions are in use for indicating the rotatory power of an active compound.

The *observed rotation* is the angle through which the plane of polarisation is turned by a layer of the liquid substance, one decimeter in thickness. Thus  $\alpha_D^{20} = 34.51^\circ$  means that the angle  $\alpha$ , through which the yellow light from a sodium flame would be turned to the right—the observer looking *against* the direction of the ray—at  $20^\circ$ , after passing through unit length of the substance, is  $34.51^\circ$ .<sup>1</sup> If the magnitude of the rotatory power be used merely to indicate the purity of the compound, or for analytical purposes, this expression is as useful as any; but for the comparison of the rotations shown by a given substance under different conditions—of temperature, for instance—it would not be satisfactory, and since Biot's early experiments seemed to show that change of temperature only affected rotation in proportion to the expansion produced, and also that the rotation of a dissolved substance was proportional to its concentration, he introduced the idea of *specific rotation*, which he supposed to be an invariable constant not dependent on the condition of the substance (Mém. de l'Acad. 1835, 13, 116; Ann. Chim. Phys. 1844, [iii.] 10, 18). The specific rotation is indicated by the symbol  $[\alpha]$ , and for

a homogeneous liquid  $[\alpha]_D^t = \frac{\alpha_D^t}{d}$ , where  $\alpha$  is the observed rotation for the D line at the temperature  $t^\circ$ , and  $d$  is the density of the substance at  $t^\circ$  as compared with water at  $4^\circ$ , as unity.

In the case of a dissolved active compound the strength of the solution must be taken account of, and may be expressed in several ways, the two commonest being as concentration and as percentage composition. Concentration,  $c$ , indicates grams of substance per 100 c.c. of solution, the substance being weighed into a graduated flask which is then filled up to some definite volume with the solvent. Then

$[\alpha]_D^t = \frac{\alpha_D^t}{c}$ . This method, however, is open to

the objection that the concentration may, and usually does, vary with change of temperature. In the second case, both active substance and solvent are weighed. The percentage composition,  $p$ , is then the weight of substance in 100 grms. of the mixture, and is, of course, independent of the temperature. In this case,

$$[\alpha]_D^t = \frac{\alpha_D^t}{p \times d}.$$

According to Biot, the specific rotation is 'the angle of rotation which a liquid would show if it contained in a volume of one cubic centimetre, one gram of active substance, and should act on the polarised ray through a column one decimetre in length,' but it is simpler to define it as the rotation which would be shown by 10 grms. of the homogeneous substance, or that quantity of solution which contains 10 grms. of it in a tube of 1 sq. cm. cross section, just long enough to contain it. The specific rotation, however, contrary to Biot's early expectations, is by no means necessarily constant, but may vary greatly with temperature, nature of the solvent and concentration.

It is scarcely to be expected that the rota-

tions of different compounds can be compared simply for 10 grms. of each, so the molecular rotation is usually calculated in such cases

$$[M]_D^t = \frac{[\alpha]_D^t \times M}{100}.$$

It is the rotation produced by one-tenth of a gram molecular weight of a homogeneous substance, or that quantity of a solution which contains one-tenth of a gram molecular weight, in a tube of one square centimetre cross section just long enough to contain it. This supposes the rotation to be proportional to the whole weight of the molecule, and Guye has suggested that since one looks through the molecule it might perhaps be better to take the rotation as proportional to its diameter, and therefore he introduced the idea of molecular

deviation,  $[\delta]_D^t = \alpha_D^t \sqrt{\frac{M}{d}}$ , but so far it cannot

be said that the regularities discovered by the use of this formula are any better than those derived from the molecular rotation, and as it involves greater trouble in calculation it has not been very much used (Compt. rend. 1893, 116, 1454).

### III. QUANTITATIVE.

*Rotation and chemical constitution.* Although Biot, in his later work, discovered that the rotation of an active compound was a property much more sensitive to external conditions than he had originally imagined, little notice was taken of the fact, and, in consequence, many of the older data, in the collection of which considerations of temperature, solvent, concentration and even the light used, were ignored, are rendered practically useless. Within the last quarter of a century, however, these factors have received greater attention, and when, for want of a better plan, the rotation values are all taken at one definite temperature, a few regularities appear between the rotation data and the chemical constitution of homogeneous liquid substances.

It is perhaps natural to take first the changes which occur in passing from member to member of a homologous series.

TABLE I.—ROTATION VALUES OF THE L-MALATES.

	$[\alpha]_D^{20}$	$[M]_D^{20}$
Malic acid <sup>1</sup>	+ 5.89°	+ 7.89°
Methyl malate <sup>2</sup>	- 6.85	- 11.10
Ethyl malate <sup>2</sup>	- 10.18	- 19.35
n-Propyl malate <sup>2</sup>	- 11.62	- 25.32
i-Propyl malate <sup>2</sup>	- 10.72	- 26.38
Amyl malate <sup>2</sup>	- 9.92	- 27.19
Capryl malate <sup>2</sup>	- 6.92	- 24.77

TABLE II.—ROTATION VALUES OF THE TARTRATES.

	$[\alpha]_D^{20}$	$[M]_D^{20}$
Tartaric acid <sup>4</sup>	- 0.30°	- 0.45°
Methyl tartrate <sup>5</sup>	+ 2.07	+ 3.68
Ethyl tartrate <sup>5</sup>	+ 7.74	+ 15.95
n-Propyl tartrate <sup>6</sup>	+ 12.68	+ 29.66
n-Butyl tartrate <sup>6</sup> [19°]	+ 10.30	+ 26.09

<sup>1</sup> Extrapolated from data by Schneider (Annalen 1881, 217, 257) from aqueous solutions.

<sup>2</sup> Walden, Zeitsch. physikal. Chem. 1895, 17, 245.

<sup>3</sup> Anschütz and Reiter, *ibid.* 1895, 10, 415.

<sup>4</sup> From data by Thomsen, J. pr. Chem. 1885, [ii.] 32, 213.

<sup>5</sup> Patterson, Chem. Soc. Trans. 1904, 85, 765.

<sup>6</sup> Freundler, Bull. Soc. chim. 1894, [iii.] 11, 305.

<sup>1</sup> Often the rotation observed in any tube is called the 'observed rotation,' the length of tube being specified.



TABLE III.—ROTATION OF VARIOUS ESTERS DERIVED FROM GLYCERIC ACID.<sup>1</sup>

	A Glycer- ate [M] <sub>D</sub> <sup>15</sup>	B Diacetyl- glycerate [M] <sub>D</sub> <sup>15</sup>	A-B	C Dimethoxy- propionate [M] <sub>D</sub> <sup>15</sup>	A-C
Methyl	-5.76°	-24.56°	18.8°	-103.8°	98°
Ethyl	-12.30	-35.56	23.26	-114.4	102.1
<i>n</i> -Propyl	-19.15	-45.17	26.06	-122.5	103.3
<i>sec</i> -Propyl	-17.49	-41.69	24.20	—	—
<i>n</i> -Butyl	-21.37	—	—	-124.2	102.8
<i>iso</i> -Butyl	-23.05	-50.38	27.33	—	—
<i>n</i> -Heptyl	-23.05	-47.89	24.84	-127.0	104.8
<i>n</i> -Octyl	-22.28	-47.92	25.64	-125.6	103.3

TABLE IV.

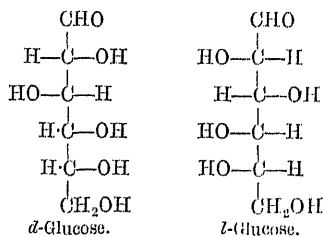
	[M] <sub>D</sub> <sup>20</sup>
Menthyl formate	-146.3°
" acetate	157.3
" propionate	160.2
" <i>n</i> -butyrate	157.1
" <i>n</i> -valerate	157.3
" <i>n</i> -caproate	157.7
" <i>n</i> -heptylate	157.7
" <i>n</i> -caprylate	155.8

TABLE VI.—ROTATION OF ESTERS OF VARIOUS ACIDS<sup>2</sup> (temperature approximately 20°).

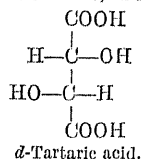
Ethyl	[M] <sub>D</sub>	Ethyl	[M] <sub>D</sub>	Ethyl	[M] <sub>D</sub>	Ethyl	[M] <sub>D</sub>
Lactate	-12.2°	Glycerate	-12.3°	Malate	-19.8°	Tartrate	+15.86°
Acetyl- lactate	-79.7	Diacetyl- glycerate	-35.6	Acetyl- malate	-52.3	Diacetyl- tartrate	+10.0
Benzoyl- lactate	+59.0†	Dibenzoyl- glycerate	+89.2	Benzoyl- malate	-11.4	Dibenzoyl- tartrate	-123.6
Methoxy- propionate	-118.9	Dimethoxy- propionate	-114.4	—	—	—	—
Methyl		Methyl		Methyl		Methyl	
Lactate	-8.6	Glycerate	-5.8	Malate	-11.1	Tartrate	+3.8
Methoxy- propionate	-112.7	Dimethoxy- propionate	-103.8	Methoxy- succinate	-92.4	Dimethoxy- succinate	+180.0†

Tartaric acid, Table II., behaves similarly, but in an opposite sense, for although it itself and its salts in aqueous solution as well as its simple esters in the homogeneous state, have a positive rotation and it is called *d*-tartaric acid, it would nevertheless give, if it could exist in the liquid homogeneous condition, a negative rotation.

2. Although to the names of many compounds the letters *d*- and *l*- are prefixed merely to indicate the sign of their rotation, Emil Fischer has been able to trace a genetic relationship between many substances related to the sugars, and prefixes the letters *d*- and *l*- to the names of compounds according to the structural relationship which they bear to glucose. In a long series of researches, pre-eminent alike for manipulative skill and reasoning power, Fischer has shown that natural glucose must have one or other of the structural formulæ :



and as it is hardly probable that we shall ever be able finally to discriminate between these, he has made the above arbitrary selection. *d*-Tartaric acid must then be, as he has shown,

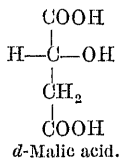


the two upper asymmetric carbon atoms of the

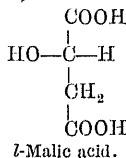
<sup>1</sup> For references see P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 865.

<sup>2</sup> From P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 867, which see regarding data marked thus †.

glucose molecule corresponding with the two asymmetric atoms of tartaric acid. For *d*-malic acid the formula is

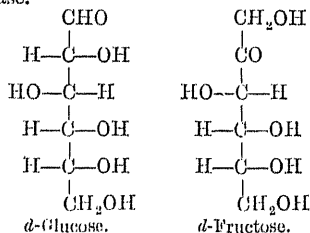


and the structure of its isomeride, ordinary natural *l*-malic acid, will be represented by



(Ber. 1896, 29, 1377).

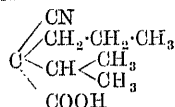
Thus, although for ethyl dibenzoyltartrate  $[\text{M}]_D^{20} = -123.6^\circ$  (Table VI.), the substance is nevertheless a *d*-compound. Similarly, fructose with a high negative rotation is *d*-fructose on account of its structural relationship with *d*-glucose, the configuration about the three lowest asymmetric carbon atoms being the same in each case.



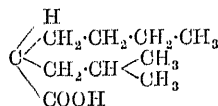
3. Table I. shows that the specific rotation of the malates becomes increasingly more negative as the series is ascended until the *n*-butyl ester is reached, and from this point the rotation rises again. There is thus a minimum (maximum negative) rotation at the *n*-propyl term. When the molecular rotation is considered, however, the behaviour is not the same, the lowest rotation occurring at the amyl term. With the tartrates, on the other hand, a maximum occurs both in the molecular, and the specific, rotation, at the same—the *n*-propyl—term. In the molecular deviation for these different esters the minimum might possibly be found at some other term. The example illustrates a kind of difficulty that often occurs; we have no criterion to decide which method of reducing the observations is the best, but the molecular rotation is probably to be preferred to the specific rotation.

This tendency to rise to a maximum and then fall again may be seen in all the data of Table III., and has been much discussed in connection with an idea put forward simultaneously by Crum Brown (Proc. Roy. Soc. Edin. 1890, 17, 181) and by P. A. Guye (Compt. rend. 1890, 110, 714; 1893, 116, 1378, 1415), who suggested that a relationship might be detected between the rotation of a compound and the masses of the four radicles attached to the asymmetric atom. Guye proposed, for

calculating the 'Product of Asymmetry,' a formula of such a character that when two of the masses became equal the expression reduced to zero. The formula predicted also the occurrence of maximum rotations at definite members of certain series, and in some cases maxima were found at, or about, these terms. But for the most part it failed entirely; the rotation of a compound does not become zero merely because two of the groups attached to the asymmetric atom are equal in weight. Fischer and Flatau (Ber. 1909, 42, 2981) have shown that, for instance, the isomerism between *n*-propyl and *sec*-propyl is sufficient to render them different groups so far as an asymmetric carbon atom is concerned. Thus *n*-propyl-*sec*-propyl—cyanoacetic acid



was found to have a rotation  $[\alpha]_D^{20} = +11.3^\circ$  in toluene solution  $p=10.4$ , and *n*-butyl-*iso*-butyl-acetic acid



had in the homogeneous state  $[\alpha]_D^{22} = +5.73^\circ$  (Fischer, Holtzapfel and v. Gwinner, Ber. 1912, 45, 247), and *n*-propyl-*sec*-propyl carbinol has  $[\text{M}]_D^{20} = +24.7$  (Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624, Table V.).

4. Tables I., III. and V. show that the molecular rotation alters most rapidly in passing through the lower members of a homologous series, a comparative constancy being reached in the higher representatives. These are examples of a regularity first pointed out by P. F. Frankland and MacGregor (Chem. Soc. Trans. 1896, 69, 121), namely, that when substitution takes place in a molecule at a point remote from the asymmetric atom, with but little change in rotatory power. Tschugaeff gives the data of Table IV. to show that: 'In every series of homologous derivatives of any asymmetric substance there occurs, at least within certain limits, an inverse proportionality between the values of the specific rotation and the corresponding molecular weight' (Ber. 1898, 31, 366). To these may be added the data by Pickard and Kenyon in Table V. According to Frankland, the general behaviour, especially the existence of a somewhat indistinct and irregular maximum, may be explained thus: 'According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return upon itself, and, beyond this, further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to

an increase in the rotatory power' (Chem. Soc. Trans. 1899, 75, 368; 1912, 101, 658).

TABLE VII.—ROTATION OF SUBSTITUTED ETHYL TARTRATES.

(Ethyl tartrate,  $[M]_D^{20} = +15.86^\circ$ .)

Substituent	$[M]_D^{20}$	Substituent	$[M]_D^{20}$
Monoc-acetyl	+23.1 <sup>10</sup>	Di-acetyl	+9.9
" monochloro-		" monochloro-	
acetyl	32.3	acetyl	+25.5
" trichloro-		" trichloro-	
acetyl	54.7	acetyl	+67.1
" phenacetyl	98.5	" phenacetyl	+79.2
" benzoyl	61.4	" benzoyl	-247.1
" o-toluy	38.2	" o-toluy	-266.5
" m-toluy	44.0	" m-toluy	-306.3
" p-toluy	63.5	" p-toluy	-484.4
" nitro	89.23	" nitro	+80.45
" m-nitro-		" m-nitro-	
benzoyl	44.38	benzoyl	-357.3

5. A regularity emerging from the data of Table VII. was first pointed out by McCrae and Patterson (Chem. Soc. Trans. 1900, 77, 1108). One acyl group, introduced into the molecule of ethyl tartrate, brings about in each case a considerable increase of rotation, whilst the introduction of a second (with the one exception of the trichloroacetyl derivatives) causes a diminution, which for the purely aromatic radicles, benzoyl and the toluyis, is very great indeed, the positive rotation of the mono-substitution product being changed into a very high negative rotation.

6. Another question that has attracted attention relates to the effect upon rotation of the presence of multiple bonds. It is often asserted that a double bond raises the rotation, but as the following figures show this general statement requires qualification.

TABLE VIII.

	$[M]_D^{20}$
Menthyl ester of	(Alcoholic solution $\alpha=0$ )
Butyric acid	. . . -164.7 <sup>10</sup>
Crotonic "	. . . 203.1
$\Delta^{\alpha\beta}$ -Pentenoic acid	. . . 177.1
$\Delta^{\beta\gamma}$ " "	. . . 172.5
$\Delta^{\gamma\delta}$ " "	. . . 160.2
$\Delta^{\alpha\beta}$ -Hexenoic	. . . 172.4
$\Delta^{\beta\gamma}$ " "	. . . 164.1
$\Delta^{\gamma\delta}$ " "	. . . 153.5
$\Delta^{\delta\epsilon}$ " "	. . . 154.4
$\Delta^{\alpha\beta}$ -Heptenoic	. . . 175.5

(Rupe, Annalen, 1903, 327, 166).

The double bond exerts a greater effect the nearer it is to the asymmetric centre. Menthyl butyrate has, almost exactly, what Tschugaeff calls the constant molecular rotation for the menthyl esters, but when a double bond is introduced into the molecule to give menthyl crotonate, the rotation is very markedly augmented, the same thing on a smaller scale being noticeable for the other unsaturated acids in which the double bond is in the  $\alpha\beta$ -position. As the double bond moves further from the asymmetric centre the rotation gradually reverts to the normal value, the behaviour being thus in

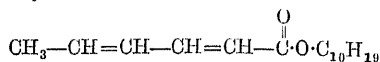
<sup>1</sup> Patterson and Davidson, Chem. Soc. Trans. 1912, 101, 378.

<sup>2</sup> In 9 per cent. methyl alcoholic solution, Frankland, Heathcote and Harger, *ibid.* 1904, 99, 1578.

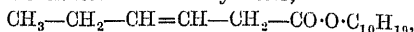
<sup>3</sup> In homogeneous; Frankland and Harger, *ibid.* 1904, 85, 1578.

accordance with the regularity of Frankland and MacGregor already alluded to under 4.

Rupe has also shown that the rotation of menthyl sorbate



$[\alpha]_D = -88.53^\circ$ , is much higher than that of  $\Delta^{\beta\gamma}$ -hexenoic acid menthyl ester,



$[\alpha]_D = -65.11^\circ$ , which he attributes to the presence of a system of alternate single and double bonds, such as has been called by Thiele, conjugated, the menthyl sorbate containing a set of three conjugated double bonds.

No perfectly general rule regarding the influence of double bonds can be formulated, however; thus it has been shown by Frankland and O'Sullivan (Chem. Soc. Trans. 1911, 99, 2327) that, whereas the rotation of propyl menthoxyacetate is less than that of allyl menthoxyacetate at  $20^\circ$ , it is greater at a temperature of  $100^\circ$ , whilst at about  $38^\circ$  the rotations of the two substances are equal. The effect of multiple bonds has been examined in a number of cases by Hilditch (*ibid.* 1909, 95, 1581).

In regard to the relative influences upon rotatory power which a substituent exerts in the *ortho*, *meta*, and *para* positions respectively, it has generally been found that the *para* di- has the greatest rotation and the *ortho* the least, whilst the phenyl derivative usually comes in between the *ortho* and the *meta* compounds (P. F. Frankland, Chem. Soc. Trans. 1896, 69, 1538; 1912, 101, 666; Cohen and Dudley, *ibid.* 1910, 97, 1737).

#### Influence of change of temperature on rotation.

The early experiments of Biot indicated that temperature played a quite unimportant part in conditioning the rotation of active bodies, but later investigations, chiefly by P. F. Frankland, have shown that, in reality, its influence is of the greatest consequence. Rotation may increase or diminish with change of temperature, or it may appear to remain almost unaffected, but it is probable that when examined over a sufficient range, the rotation of an active compound will show a maximum or a minimum value, or perhaps several such. An idea of the behaviour met with will be obtained from Figs. 34 and 35, the former of which represents the influence of temperature change upon the molecular rotation of a number of closely related substances.

Menthyl tartrate (see figure) is positive at  $20^\circ$ , but below this temperature its rotation becomes negative; it therefore furnishes an example of a compound whose rotation passes through the point of inactivity at some definite temperature for light of a particular wave length. The rotation of ethyl tartrate is higher than that of the menthyl ester and the increase of rotation on heating is somewhat greater. The point of inactivity would be reached about  $-34^\circ$ . Curves for the *n*-propyl, *sec*-propyl, *iso*-butyl, *iso*-amyl, *sec*-octyl and *amyl* esters are also shown. The curves are, in general, alike, but even for such closely similar substances, the institution of comparisons between the rotation values at any one given temperature cannot yield very

satisfactory results. The rotation values for these esters at 20° would not be in the same sequence as at, say, 180°. At the former

*Temperature Rotation Curves for Various Esters of Tartaric Acid.*

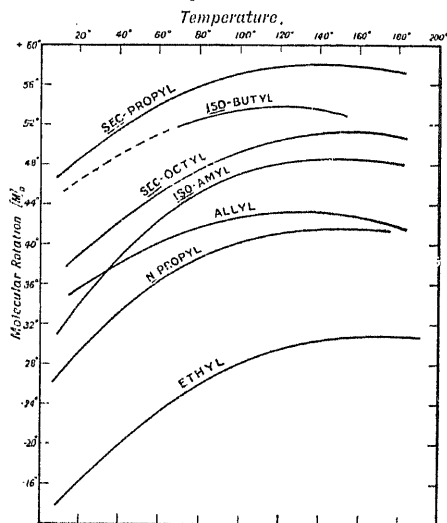


FIG. 34.

temperature, for instance, allyl tartrate has a higher rotation than has iso-amyl tartrate, whereas at the latter the reverse is the case. Other examples are obvious.

The curves of Fig. 35 refer to a number of compounds not so intimately related. The

*Temperature Rotation Curves for Various Esters.*

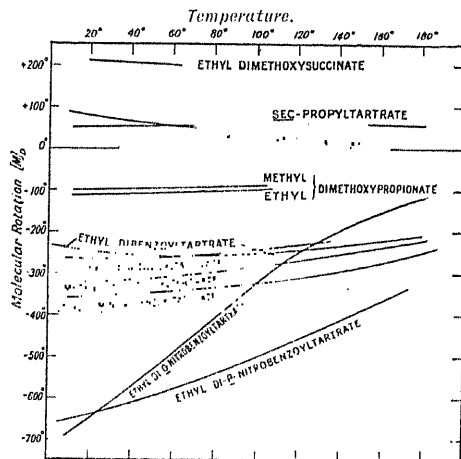


FIG. 35.

scale of the rotations is very much smaller, the curve for *sec*-propyl tartrate of Fig. 34 being included for comparison.

The uppermost curve represents the behaviour of ethyl dimethoxysuccinate, the rotation of which,  $[M]_D^{20} = +210.0^\circ$ , falls to  $199.8^\circ$  on

heating to 60°. With this may be compared the curves for the methyl and ethyl esters of dimethoxypropionic acid, which have rotations at 20° of about  $-100^\circ$ , becoming less negative as the temperature rises. These dimethoxypropionates are derived from *l*-glyceric acid which, in its configuration, corresponds to *d*-tartaric acid, so

*d*-tartaric acid, would have of about  $+100^\circ$ , gradually of temperature, and would

thus show a behaviour closely analogous to that of the dimethoxysuccinates, which with two asymmetric centres have a rotation almost twice as great. The other curves on the diagram represent data obtained by P. F. Frankland and his pupils, and exhibit the very great effect which change of temperature may exert. That for ethyl dibenzoyltartrate is of especial interest as it shows a minimum of  $-258^\circ$  at a temperature of 63° (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1587). It was the first recorded instance of this phenomenon, but a considerable number of other cases have since been found. All the curves in Fig. 34 show distinct maxima, and maxima also exist in the temperature-rotation curves for ammonium and sodium malate, and potassium tartrate (Grossmann and Pötter, *Ann.* 1896, 289, 111). for solutions of sodium and potassium tartrates, for some of the potassium alkyl tartrates (Patterson, Chem. Soc. Trans. 1904, 85, 1116) and for homogeneous menthol (Patterson and Taylor, *ibid.* 1905, 87, 33) and in other cases.

The curves represent the results of Frankland and Wharton (Chem. Soc. Trans. 1896, 69, 1309, 1583) and Frankland and Harger (*ibid.* 1904, 85, 1571). That for ethyl dibenzoyltartrate is very like the graph for ethyl di-*m*-nitrobenzoyltartrate and whilst those for ethyl di-*m*-nitrobenzoyltartrate and ethyl di-*p*-nitrobenzoyltartrate are again very similar. The rotation of ethyl di-*o*-nitrobenzoyltartrate is most remarkable. The very high negative rotation diminishes with surprising rapidity as the temperature rises, and appears to have a point of inflection somewhere between 80° and 100°. The degree in which relationship between rotation and constitution depends on the temperature of comparison is strikingly apparent from this set of substances. At a low temperature, the *o*-nitrobenzoyl derivative has the greatest negative rotation, whilst at a temperature of 135° it would have the lowest, its graph cutting the other curves at intermediate temperatures. Nevertheless it is probably of the same type as the others. The rotation of ethyl dibenzoyltartrate is a minimum at 63°, and it seems likely that the di-*o*-toluyl derivative will reach a minimum value at a somewhat lower temperature, and similarly for the *m*-nitrobenzoyl derivative. The slope of the curve for ethyl di-*p*-nitrobenzoyltartrate is greater, and therefore its minimum should lie at a still lower temperature. Similarly, the last curve may also have a minimum of high numerical value at an even lower temperature. On the other hand, the di-*o*-nitrobenzoyl derivative may rise to a maximum, and it is probable that ethyl di-*p*-nitrobenzoyltartrate and the other esters also have maxima at successively higher

temperatures. If this be true, the variation of the rotation of an active compound with change of temperature is a *periodic* phenomenon, and several maxima and minima might be expected to occur as one or other of the groups attached to the asymmetric atom preponderates. Unfortunately  $\therefore$  to examine the variation over a wide range of temperature.

Attempts are often made to express mathematically the relationship between rotation and temperature, the parabolic equation

$$a = a + bt + ct^2,$$

being usually applied. If the above be true, however, this form cannot be the correct one to use; if it were, the rotation would not be a periodic function, but should proceed towards infinity both at low and at high temperatures, and the two limbs of the curve ought to be of exactly the same shape. Winther (Zeitsch. physikal. Chem. 1902, 41, 176) has calculated such an equation for ethyl tartrate and reduced it to the form

$$[\alpha]_D^t = 14.126 - 0.000401[t - 149]^2,$$

the temperature 149° being that of the maximum rotation. He suggested that the value of the specific rotation should be reckoned, not from zero, but from this maximum value, such a datum to be called the 'rational specific rotation,'  $[A]_D^t$ .

$$[A]_D^t = a - [\alpha]_D^t = b[t - 149]^2$$

(*l.c.* 207).

Winther assumes that the temperature at which the maximum occurs is the same at least for the three esters with which he deals, but this is not the case (Patterson, Chem. Soc. Trans. 1908, 93, 1844). The curves of Fig. 34 show maximum rotations at temperatures as below.

TABLE IX.

Ester	Temperature	Maximum $[M]_D$
Ethyl tartrate	175°	+30.9°
<i>n</i> -Propyl "	150	41.65
<i>sec</i> -Propyl "	144	58.03
<i>iso</i> -Butyl "	120	53.9
<i>iso</i> -Amyl "	151	48.72
Allyl "	130	43.24
<i>sec</i> -Octyl "	160	51.46

It may be, however, that the maximum rotations occur at 'corresponding' temperatures at which it would be legitimate to compare with one another the rotation values of different active compounds, or that comparison should be made at temperatures connected in some simple manner with those at which the maxima occur. A suggestion of this sort was made by Patterson (Chem. Soc. Trans. 1904, 85, 765), based on the fact that the rotations of methyl, ethyl, and *n*-propyl tartrate would respectively become zero at 0°, -34°, and -60°; these may be 'corresponding' temperatures, and, as a first approximation, the rotations, of methyl tartrate, of ethyl tartrate, and of *n*-propyl tartrate may be directly comparable at T°, (T-34°), and (T-60°) respectively. The ratio of the rotations of the esters thus obtained remained nearly constant over a fairly wide

It may be added that when turpentine was converted into vapour it still retained its optical

power (Biot, Ann. Chim. Phys. 1819, [ii.] 10, 73), and the same thing has been observed for certain derivatives of amyl alcohol (Guye and do Amaral, Arch. sc. phys. Genève, 1895, [iii.] 33, 409, 513; Compt. rend. 1895, 120, 1345; Wied. Beibl. 1895, 19, 792, 894).

*Influence of pressure on rotation.* To determine the influence of pressure on rotation is very difficult, since the pressure applied to the liquid must also be applied to the end discs of the containing tube, when they too become double refracting and optically active. In the one investigation which has been carried out on the subject, L. H. Siertsema (Arch. Néerl. Sci. 1899, [ii.] 2, 29; 1900, [ii.] 3, 79) found it necessary to immerse the polarising and analysing prisms in the liquid to be examined and submit them as well as the liquid to the pressure. It was found, for instance, that the rotation, 12.4°, of a decimetre layer of a cane sugar solution  $c=18.7$ , was only altered by about 0.31° per one hundred atmospheres increase of pressure. (These figures are calculated from the numbers in the tables given by Siertsema.)

*Rotation in solution.* The rotation of an active compound in solution in an inactive liquid is usually different, and often very greatly different, from its rotation in the homogeneous condition. The behaviour of ethyl tartrate on dilution with water illustrates this well. The rotation of the homogeneous ester, at 20° ( $l=1$  decimeter), is 9.4°, and if the tube were extended to twice its original length, without alteration of the cross section, water being added to fill up the resulting space, the rotation of the 2 decimeter layer of solution, after thorough mixing, would be 20.4°, or more than twice as much as before. If the tube were again doubled in length and more water added, the rotation would become 27.6°, and on continuing the process until the tube could be considered infinitely long, a rotation of 32.3° would ultimately be reached.

The curves shown in Fig. 36 represent the effect of several solvents of very different character, not upon the observed, but upon the specific rotation of this ester, at 20°. For pure homogeneous ethyl tartrate  $[\alpha]_D^{20} = +7.8^\circ$ , and this increases on mixture with water in such a manner as to reach the value +26.84° in an extremely dilute solution. In nitrobenzene, the increase of rotation is something the same as in water but the curve is different in shape and the effect of the solvent is greater, the rotation in very dilute solution being raised to +41°. In ethyl alcohol, the rotation diminishes slightly to reach a minimum value at a concentration of  $p=60$ , after which it increases to a final value of +9.13°. The behaviour of benzaldoxime is very remarkable: the rotation of the ester increases until  $p=70$ , at which point a maximum value of +13.6° is reached. Further addition of oxime then diminishes the rotation, so that at  $p=22$  the solution becomes inactive, and at infinite dilution the specific rotation would be approximately -16°. The rotation therefore varies 30° between the extreme limits, and by about equal amounts on either side of zero (Chem. Soc. Trans. 1907, 91, 508). In acetylene tetrabromide the rotation of the dissolved ethyl tartrate diminishes very

rapidly with diminution of concentration, the rotation varies as the dilution increases, to a value of  $-20^\circ$ .

Thus the rotation of this ester, whose specific rotation in the pure condition is only  $+7.8^\circ$ , can be made to vary from  $+41^\circ$  to  $-20^\circ$  by

*Influence of Various Solvents on the Rotation of Ethyl Tartrate.*

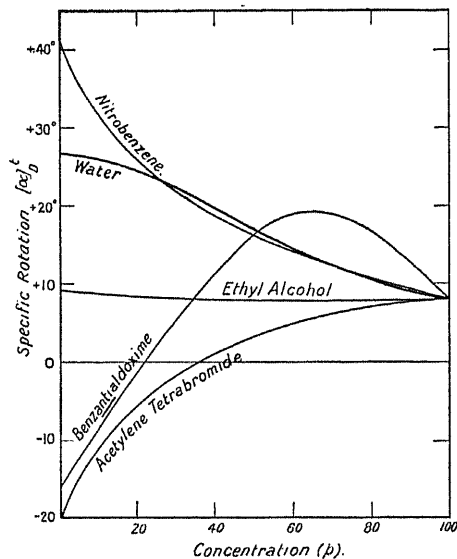


FIG. 36.

solution in these solvents; clearly, therefore, care must be taken in reporting the exact circumstances under which any rotation has been measured, and also in utilising rotation data obtained by the use of several different solvents. The curves also show that if an active compound is solid, so that its rotation in the homogeneous liquid condition cannot be determined, this value may still be arrived at by extrapolation from the data for its solutions, and, for a number of solvents, the accuracy with which the extrapolation could be made depending, of course, on the solubility of the compound.

Many attempts have been made to explain these remarkable effects. Naturally a correlation has been suggested between the rotation and the osmotic molecular weight of the dissolved substance, but it has proved impossible up to the present to establish any connection. (See Frankland and Pickard, *Chem. Soc. Trans.* 1896, 69, 131; Patterson, *ibid.* 1901, 79, 182; 1902, 81, 1111; Ber. 1905, 38, 4049; 1908, 41, 113; Patterson and Thomson, *ibid.* 1907, 40, 1244; Walden, *ibid.* 1905, 38, 389; 1906, 39, 658; 1907, 40, 2463; Purdie and Irvine, *Chem. Soc. Trans.* 1904, 85, 1055.)

Another proposal, by Tammann, was that the rotation depends upon the internal pressure of the solvent or of the mixture of solute and solvent. This idea was applied by Patterson (*Chem. Soc. Trans.* 1901, 79, 188) in the case of ethyl tartrate in various solvents, but instead of calculating the internal pressure,

the molecular solution-volume of the ethyl tartrate at infinite dilution in the different solvents was determined, the assumption being made, as a first approximation, that all the change of volume suffered in the process of solution might be attributed to the solute, and further, that the magnitude of the solution-volume might be regarded as a measure of the internal pressure. Although these assumptions are not generally admissible, it is nevertheless possible that in some instances they may be nearly fulfilled. In any case experiment discovered a parallelism between the magnitude of the specific rotation and the molecular solution-volume, both at infinite dilution, as is illustrated in the following table (Ber. 1905, 38, 4101).

TABLE X.—ROTATION AND SOLUTION-VOLUME OF ETHYL TARTRATE IN VARIOUS SOLVENTS.

(Ethyl tartrate, M.V.=170.9 c.c.)

Solvent	[M.S.V.] <sup>20</sup> infinite dilution	[α] <sub>D</sub> <sup>20</sup> infinite dilution
Water	160.1	+26.85°
Methyl alcohol	159.3	+11.50
Glycerol	163.3	+10.57
Ethyl alcohol	164	+9.13
n-Propyl alcohol	167.5	+7.40
iso-Butyl alcohol	170.3	+6.53
sec-Octyl alcohol	174.3	+5.24
Benzene	175.1	+6.1
Toluene	174.8	+4.6
o-Xylene	176.8	+2.7
m-Xylene	176.5	+1.8
p-Xylene	176.1	+0.7
Mesitylene	177.4	-3.0
Chloroform	178	-3.2

Excepting for water, there appears to be a fairly close relationship between the values of these two magnitudes. The idea was taken up by Winther and applied to explain the change of rotatory power with variation of temperature. In certain cases it is found that there is a direct, linear relationship between the values of the rotation and the molecular volume either in the homogeneous condition or in solution. Thus, for example, the figures for homogeneous ethyl tartrate may be given.

TABLE XI.

t	[α] <sub>D</sub>	Δ[α] <sub>D</sub>	v	Δv	k
56.8°	+4.37°	0.38	0.8906	0.0087	44
67.6	4.75	0.17	0.8993	0.0027	63
71.3	4.92	0.28	0.9020	0.0061	46
78.2	5.20	0.40	0.9081	0.0070	57
86.7	5.60	0.70	0.9151	0.0114	61
100	6.30		0.9265		

In the above table v is the specific volume, and k is a constant calculated from the equation:

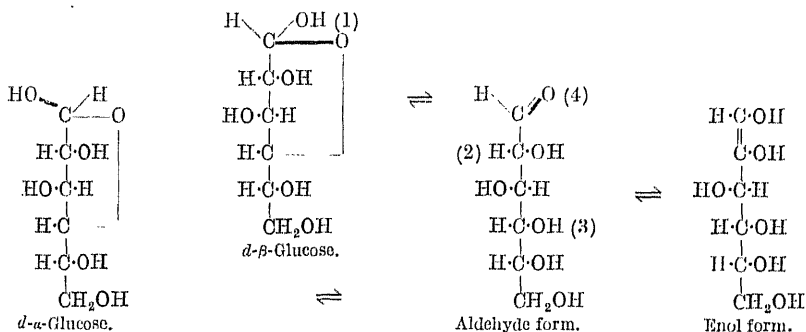
$$\Delta[\alpha]_D = k \Delta v.$$

The values of k vary irregularly about a mean value of 54, so that the rotation appears to be directly proportional to the specific volume. (For many other examples see Winther, *Zeitsch. physikal. Chem.* 1906, 55, 263.)

*Muta-rotation.* It not infrequently happens that the rotation of a compound, generally in

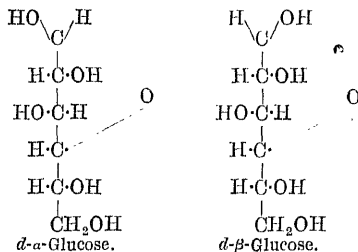
solution, starting from a certain initial value gradually falls to reach a different end value. The substances which first attracted attention in this direction belong to the class of sugars, which rendered the matter of practical importance. When *d*-glucose is crystallised from 70 p.c. alcohol at the ordinary temperature, an anhydrous product is obtained, giving when dissolved in water, an initial specific rotation of about  $+109^\circ$  which falls gradually to the constant value  $+53^\circ$ . The solid form is called *d*- $\alpha$ -glucose. If, on the other hand, glucose be crystallised from water at a temperature above  $98^\circ$ , a solid, *d*- $\beta$ -glucose, separates having a rotation initially of only  $+19^\circ$  or thereabouts, the value being a little uncertain, as the substance is difficult to prepare in a pure condition. This rotation, too, changes slowly with lapse of time and ultimately also acquires the value  $+53^\circ$ . Since the final rotation is almost half the highest value the phenomenon used to be called bi-rotation or semi-rotation, but is now generally referred to, on the suggestion of Lowry, as *muta-rotation*. A similar behaviour is found for fructose, galactose, lactose, maltose and other sugars.

The two varieties of glucose in the solid condition may be represented by the formulæ:



In solution the compound of constant rotation may have the true aldehyde formula or it might have the enolic structure, the presence of which last seems necessary to account for the readiness with which glucose in faintly alkaline solution is converted into a mixture of glucose, fructose and mannose. On dissolving *d*- $\beta$ -glucose in water, the hydrogen atom marked (1) may wander to the lactic oxygen atom, the uppermost carbon atom of the *d*- $\beta$ -glucose molecule thus losing its asymmetry to give the inactive group  $\text{H}-\text{C}=\text{O}$  of the aldehyde form.

If now this hydrogen atom passes back again from its position (3) and attaches itself to the carbon atom (4) by the bond indicated, it will yield *d*- $\alpha$ -glucose, in which the asymmetry of the uppermost carbon atom is the opposite of that found in *d*- $\beta$ -glucose. If the hydrogen atom (2) of the aldehyde form wanders to the oxygen atom (4), both of the upper carbon atoms lose their asymmetry and the enolic form results, which presumably may pass back again through the aldehyde form into *d*- $\alpha$ -glucose or *d*- $\beta$ -glucose or into the two forms of fructose or mannose respectively.



in which, however, the relative positions of the hydrogen atom and the hydroxyl group attached to the uppermost carbon atom are known.<sup>1</sup> When one of these is dissolved in water a change might take place in two essentially different ways. Emil Fischer (Ber. 1890, 23, 2626) suggested that the molecule may become hydrated, the final constant value of the rotation being that of the hydrate. Lowry, however (Chem. Soc. Trans. 1899, 75, 213; 1904, 85, 1541, 1551), from analogy with the rotation changes which take place in nitrocamphor in non-aqueous solutions, in which there can be no hydration, attributes the change to an isodynamic process or perhaps to two such processes:

#### *Influence of Temperature Change on Rotation in Solution.*

Alteration of the temperature of a solution is generally accompanied, as in the case of a homogeneous compound, by a corresponding alteration in rotation. The case of ethyl tartrate has been examined fairly completely and the curves of Fig. 37 will help to explain the results obtained; the thick graph represents the change of rotation of the undiluted ester.

In a solvent such as acetylene tetrachloride,  $p=9.3$  which, at  $20^\circ$ , has a powerful depressing effect, the rotation rises rapidly with increase of temperature, whilst in a solvent like  $\alpha$ -nitronaphthalene,  $p=5$ , which greatly raises the rotation of the ester, rise of temperature diminishes the rotation with almost equal rapidity. Other solvents, or the same solvents at intermediate concentrations, produce effects lying between these extremes, in such a manner that, roughly speaking, the whole series of curves gives the impression of a gradual variation of

<sup>1</sup> See E. F. Armstrong: The Simple Carbohydrates and the Glucosides (Longmans, 1910), p. 64.

some property irrespective of the chemical composition of the solvents. It is interesting that,<sup>2</sup> whilst the maximum rotation of the homogeneous ester lies at a temperature of 175°, it is again quite apparent in a solution in *m*-dinitro-benzene of  $\eta=49.6$ , but at a lower

*Influence of Temperature on Rotation  
in Solution  
Ethyl Tartrate in Various Solvents.*

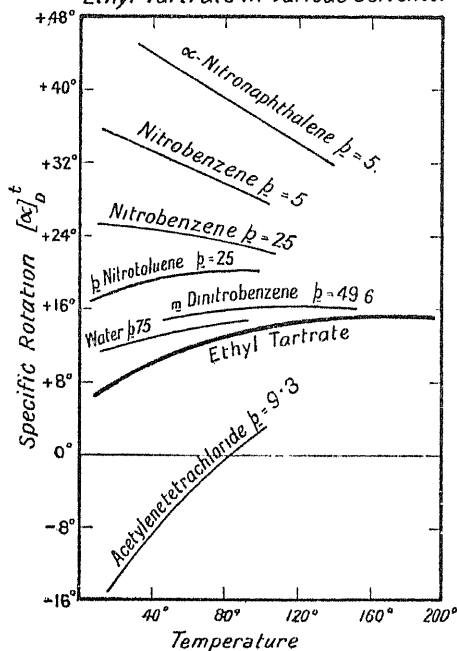


FIG. 37.

temperature, 123°. The curve for *p*-nitrotoluene,  $p=20$ , shows a maximum at about 85°, and, from the appearance of the other curves, the maximum passes rapidly to lower temperatures as the rotation increases. It seems likely that other substances closely related to ethyl tartrate would behave in solution in a very similar manner.

*Rotation of active salts in solution.* In 1873, Landolt (Ber. 1873, 6, 1077) observed that some of the neutral tartrates in aqueous solution had all very nearly the same specific rotation, whilst later, Oudemans (Annalen, 1879, 197, 48, 66) showed that the rotation of dilute solutions of salts of quinine seemed to be independent of the acid radicle. Händrich (Zeitsch. physikal. Chem. 1893, 12, 476) applied the dissociation theory to the explanation of these results, suggesting that, as the solution of a salt is diluted, the rotation is modified because the active radicle becomes more and more dissociated from, and therefore less and less influenced by, the inactive radicle. In very dilute solutions, the rotation is that, merely, of the free active ion. Thus Landolt found the following data for solutions containing 7.69 grms. of tartaric acid in 100 c.c. Even in these by no

means very dilute solutions the rotations lie fairly close together.

Neutral tartrate of	[M] <sub>b</sub>
Lithium . . .	+58.1°
Sodium . . .	59.9
Potassium . . .	64.4
Ammonium . . .	63.0

Again, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1086) give the following rotations for compounds formed by the combination respectively of dextro- and lævo-tetrahydroquinoline with dextro-camphor-sulphonic acid.

Substance	$[M]_D$
$dC_{10}H_{13}N \cdot dC_{10}H_{15}O \cdot SO_3H$	$+173.3^\circ$
$\text{—————} \cdot \text{—————}$	$-69.5$

Half the difference between these,  $121.4^\circ$ , should be the rotation of a dilute solution of either form of tetrahydroquinidine hydrochloride, and for the levo variety experiment gave  $-121.7^\circ$ . Further, half the sum of the above,  $51.9^\circ$ , should be the rotatory power of ammonium camphor sulphonate, for which the value  $51.7^\circ$  was found. The optical activity of small quantities of active bases or acids, obtained by the resolution of potentially active compounds.

The truth of this Law of Oudemans, as it is called, has been questioned by F. L. Shinn (J. Phys. Chem. 1907, 11, 201).

The following table gives some data for ethyl tartrate and for nicotine, in regard to the relative effect of the same set of solvents on the rotation of a number of different active compounds.

TABLE XII.

Solvent	Ethyl tartrate [ $\alpha$ ] <sub>D</sub> in finite dilution	Nicotine [ $\alpha$ ] <sub>D</sub> in finite dilution
Formamide . . .	+30.4°	-70°
Water . . .	26.85	77.4
Methyl alcohol . .	11.5	129.4
Ethyl alcohol . .	9.13	140.1
Benzene . . .	6.1	163.5
Ethylene bromide .	-19.1	183.5

The sequence of the rotations in these different solvents is the same for both active compounds. *See also* Walden (Ber. 1905, 38, 345) for data bearing on this subject. Further work in this direction is desirable.

*Mixed solvents.* The effect of mixed solvents such, for instance, as a mixture of nitrobenzene and ethylene bromide on ethyl tartrate, or of water and calcium chloride on glucose, has been examined by Rimbach (Zeitsch. physikal. Chem. 1892, 9, 698; Rimbach and Weber (*ibid.* 1905, 51, 473); Patterson and Montgomerie (Chem. Soc. Trans. 1909, 95, 1128); Stubbs (*ibid.* 1911, 99, 2265); Patterson and Anderson (*ibid.* 1912, 101, 1833), but no generalisation seems to be possible as yet.

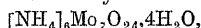
### Combination of Active Solute with Inactive Solvent.

A suggestion often made to account for the variations of rotation observed in solution in what are termed 'indifferent' solvents, is that complex molecules of solute and solvent are formed, but the evidence advanced is usually of a negative character. An extensive research



by Scheuer (Zeitsch. physikal. Chem. 1910, 72, 513), which included experiments on the viscosity, dilatation, melting-point, and rotation for light of various refrangibilities, of mixtures of ethyl diacetyltartrate, and menthol respectively, with a number of different solvents, failed to detect, either in the liquid or the solid phase, any sign of complex formation.

In some cases, however, combination certainly does occur. Thus Biot (Mém. de l'Acad. 1837, 16, 229; Ann. Chim. Phys. 1844, [iii.] 11, 82; 1850, 29, 341, 430; 1860, 59, 229) noticed that the addition of boric acid to solutions of tartaric acid greatly increased their rotation, and the same thing has been observed by Gernez for molybdates and tungstates (Compt. rend. 1887, 104, 783; 1888, 106, 1527; 1889, 108, 942). The addition of one molecular proportion of ammonium molybdate



to a  $c=2.5$  solution of tartaric acid, raises the rotation,  $\alpha_D^{17}$ , from  $+0.351^\circ$  to  $+15.66^\circ$ . This principle is therefore occasionally employed in investigations where small quantities of active compounds are obtained, in order to increase the rotation and render it perceptible. These increases have only been observed for active oxy acids, and the method must be used with caution, since it was found by Gernez (Compt. rend. 1889, 109, 769) that whilst the addition of one . . . . . rms.) of sodium . . . . . to

malic acid solution,  $c=9.97$ , raised  $\alpha_D^{17}$  from  $-0.189^\circ$  to  $+13.26^\circ$ , the addition respectively of 1.4, 2.85, 4.25 grms., gave in each instance an inactive solution, maximum and minimum rotations occurring at intermediate concentrations. Compounds of this type and also those containing arsenic and antimony have been examined by G. G. Henderson with Prentice (Chem. Soc. Trans. 1895, 67, 1035), Barr (*ibid.* 1896, 69, 1452) and Orr and Whitehead (*ibid.* 1899, 75, 548) not only with malic acid but also with lactic acid, whilst Walden (Ber. 1897, 30, 2889) uses alkaline uranyl nitrate for producing strongly active compounds of the same type.

**Rotation dispersion.** The determination of the rotation for light of different wave-lengths may be carried out either with approximately monochromatic sources of light, such as a flame containing incandescent salts of sodium, lithium, thallium, indium, or that from a mercury arc lamp, the light being purified by means of some coloured solution which absorbs the rays not required. (See, for example, Winther, Zeitsch. physikal. Chem. 1902, 41, 161; Scheuer, *ibid.* 1910, 72, 513.) It is, however, better to purify white light or that from any of the sources mentioned, by means of a spectroscope, placed at either end of the polarimeter.

Results similar to the following are then obtained:

Fraunhofer line	B	C	D	E	F	G
Wave-length	686.7	656.2	589.2	526.9	486.1	430.7
Quartz <sup>1</sup> $\alpha$						
[1 mm.]	+15.75°	17.31°	21.71°	27.54°	32.76°	42.50°
Sucrose <sup>2</sup> $\alpha$	+47.56	52.70	66.40	84.56	101.81	131.96

The ratio of the values for light of any two

<sup>1</sup> Sorret and Sarasin, Compt. rend. 1882, 95, 635.

<sup>2</sup> Cane sugar in water,  $p=10-30$ , Stefan, Wien. Sitz. Ber. 1866, 52, II. 486.

wave-lengths is termed the dispersion coefficient, and in the above cases, taking the B line as unit, the dispersion coefficients would be as follows:

Fraunhofer line	B	C	D	E	F	G
Quartz	1	1.09	1.38	1.75	2.08	2.70
Sucrose	1	1.11	1.40	1.78	2.13	2.77

The dispersion of quartz is practically the same as that of a cane sugar solution—a sucrose solution which has the same rotation as a certain quartz plate for any one ray will have the same rotation as the quartz plate for all rays, which makes it possible to use quartz plates in the rotation instruments for the rotation of sugar solutions.

For the relationship between the rotation and the wave-length of the light used, Boltzmann (Pogg. Ann. Jubell. 1874, 128) has proposed the equation

$$\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^2},$$

in which, from the above observations on quartz,  $A=7.108293 \times 10^{-6}$  and  $B=0.1477086 \times 10^{-12}$ . For the sugar solution  $A=2.16036 \times 10^{-5}$  and  $B=5.47276 \times 10^{-13}$ . Winther (Zeitsch. physikal. Chem. 1902, 41, 182) suggests another expression, which agrees better with his results for esters of tartaric acid and may prove to be of a more suitable form.

In a number of compounds such as quartz, and in sucrose solutions, the dispersion coefficients do not vary with change of temperature, and in numerous cases also the dispersion coefficients are the same for the homogeneous active substance as for its homologous esters. Dispersion is said to be normal. Sometimes, however, as was first observed for solutions of tartaric acid by Biot (Mém. de l'Acad. 1838, 15, 93), the magnitude of the rotation does not increase with the wave-length of the light, but reaches a maximum at some intermediate wave length and then decreases again. Winther (Zeitsch. physikal. Chem. 1902, 41, 177) finds this to occur also in homogeneous compounds, such as the methyl, ethyl and *n*-propyl esters of tartaric acid and the same holds for ethyl diacetyltartrate (Scheuer, *ibid.* 1910, 72, 587).

Fig. 38 represents data obtained by Winther (*l.c.*) for the first three simple esters of tartaric acid, at a number of different temperatures, the dispersion being abnormal in all cases. The maximum rotation for methyl tartrate occurs in the neighbourhood of the yellow light, but as the temperature rises the maximum shows a tendency to shift towards the violet; this is clearly more pronounced amongst the curves for ethyl tartrate, and so much so in those for *n*-propyl tartrate that at  $70^\circ$  the dispersion has almost become normal. It is of interest that, just as has already been observed in regard to the effect of temperature change on rotation in solution (Fig. 37), the set of curves for these three homologous esters seems to form a complete whole; some property appears to progress gradually throughout the diagram, irrespective of the nature of the chemical compound used. The alteration of dispersion for the three esters is closely analogous, so that if methyl tartrate be heated until it has a rotation of, say,  $\alpha^\circ$  for the red rays, its dispersion curve at that temperature will be the same as that for ethyl tartrate

at the temperature at which its rotation is also  $\alpha^\circ$  for red light, the same curve being obtained for *n*-propyl tartrate at some other temperature. The dispersion curve for ethyl tartrate, for example at  $72^\circ$ , is coincident with the dispersion curve for *n*-propyl tartrate at  $19^\circ$ ; so far as this property is concerned, ethyl tartrate at  $72^\circ$

Rotation Dispersion of Methyl, Ethyl and *n* Propyl Tartrate at Different Temperatures.

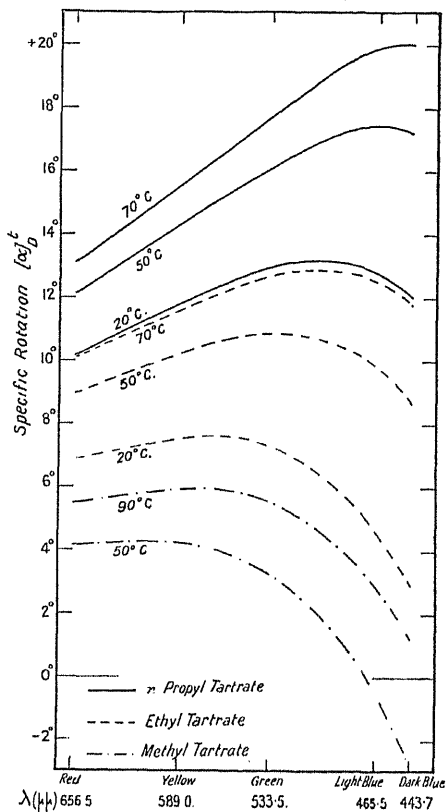


FIG. 38.

seems to be the same thing as *n*-propyl tartrate at  $19^\circ$ .

For a photographic method of determining dispersion into the ultra-violet, see Lowry, Proc. Roy. Soc. 1908, A. 81, 472.

**Magnetic rotation.** Faraday discovered in 1845 that the plane of polarisation of light passed through transparent matter of any kind in a magnetic field in the direction of the lines of force, is altered to an extent proportional to the strength of the field, the thickness of the layer of substance traversed, and the nature of the light used. If the field is produced by a current flowing round a coil, the direction of rotation of the plane of polarisation is generally positive for diamagnetic substances and negative for magnetic substances, the positive direction being that in which the current producing the field flows, without reference to the direction of the ray. Thus if the field be produced by a current flowing in the counter-clockwise direction relative to the observer, the rotation of a

positive substance will be also in a counter-clockwise direction, and if the beam be reflected by the substance the plane of polarisation will gain deflected in the same direction, so that the angle of rotation after passing back and forwards through the substance will be doubled. Magnetic rotation thus differs very markedly from permanent rotation.

From the chemical point of view this phenomenon has been developed almost exclusively by the late Sir W. H. Perkin, in a series of very comprehensive papers (Chem. Soc. Trans. 1882, 41, 330; 1884, 45, 421; 1896, 69, 1025; 1906, 89, 608; 1907, 91, 806 and others).

Perkin's method consists in determining the magnetic rotation of water and then under the same circumstances of field, &c., the magnetic rotation of some other substance, the current being reversed after each observation and the mean of the sum taken. Each rotation is then divided by the corresponding density, the value thus found for the substance as compared with that for water taken as unity being the specific magnetic rotation of the substance. The specific rotation multiplied by the molecular weight gives the molecular magnetic rotation.

In ascending series, the molecular magnetic rotation is a constant amount for each  $\text{CH}_2$  group added, and definite values may be obtained for certain groups or atoms so that, knowing the constitution of a compound, its molecular magnetic rotation can be calculated. Perkin applied this method as a criterion for the determination of the constitution of certain substances which presented difficulty. Thus, for example, he found (Chem. Soc. Trans. 1902, 81, 294)

Substance	Molecular magnetic rotation
Hexane	6.646
Hexamethylene	5.664

the difference between these values ( $-0.982$ ) being that due to ring formation and loss of two atoms of hydrogen. In his last paper (*ibid.* 1907, 91, 807) he quotes:

Magnetic rotation of hexatriene	12.196
Difference due to ring formation	$-0.982$

11.214

The sum, 11.214, should be the rotation of benzene, which is, in fact, 11.284. There is little doubt that magnetic rotation is one of the most definitely constitutive properties that we know, but, owing to the elaborate and costly character of the apparatus required and the unremitting attention necessary in carrying out observations, it has been used by few other workers.

In addition to the original papers quoted in this article, the following books may be consulted for fuller details regarding most of the matters dealt with:—H. Landolt, Das optische Drehungsvermögen organischer Verbindungen, 1898; the same, translated, with additions to date, by J. H. Long, The Optical Rotating Power of Organic Substances, 1902; J. H. van't Hoff, The Arrangement of Atoms in Space, translated by A. Eilhart, 1898; A. Werner, Kurzes Lehrbuch der Organischen Chemie, 1904; A. W. Stewart, The

T. S. P.

**POLIANITE v. PYROLUSITE.****POLONIUM** (*Radium F*; *Radiotellurium*).

At. wt. = approx. 210 (?).

A radioactive element, discovered by P. and M. Curie in the residues obtained from pitchblende after the mineral had been roasted with sodium carbonate and the product extracted with sulphuric acid to dissolve uranium salts. The insoluble residue, from which radium was originally prepared, was found to contain another radioactive element which was precipitated together with bismuth sulphide by sulphuretted hydrogen in acid solution (Compt. rend. 1898, 127, 175). The further separation of the active body from bismuth was effected by the following methods: (1) sublimation of the sulphides at 700° *in vacuo*, the active sulphide being the more volatile; (2) precipitation of the basic nitrates from solution, the active material precipitating first; (3) precipitation of a strongly acid chloride solution with hydrogen sulphide, the active sulphide separating first. (For the preparation of polonium compounds v. also Giesel, Ann. Chim. Phys. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608; 1903, 36, 728, 2368; 1908, 41, 1059; Marckwald, Ber. 1902, 35, 2285; Curie and Debierne, Compt. rend. 1910, 150, 386.)

In 1902, Marckwald (Ber. 1902, 35, 2285, 4239; 1903, 36, 2662) obtained a radioactive substance associated with tellurium, which he called *radiotellurium*. This is almost certainly identical with polonium, as Debierne soon afterwards pointed out (Compt. rend. 1904, 139, 281). *Elektronen* 1906, 1, 111. b. Radioaktiv. (Chem. Zentr. 1906, ii. 412) his material should be called polonium.

Polonium has been found in the uranium mineral carnotite (Friedel and Cumenge, Compt. rend. 1899, 128, 532).

When a plate of bismuth is immersed in a solution of the active matter is deposited on the plate; the active material is also precipitated by stannous chloride (Marckwald).

The radiation from polonium is extremely active, consisting entirely of  $\alpha$ -rays identical with those of radium (Becquerel, Compt. rend. 1903, 136, 431, 977). The rays are deflected in a strong magnetic field (Mackenzie, Phil. Mag. 1905, [vi.] 10, 538; Ewers, Chem. Zentr. 1906 i. 1084). The range of the  $\alpha$ -particles in air is 3.8 cms. (Levin, Amer. J. Sci. 1906, [iv.] 22, 8. cf. Aschkinass, Annalen Physik. 1908, [iv.] 27, 377). The activity of polonium decays according to the usual exponential law, the half-period being 140 days (Curie, Compt. rend. 1906, 142, 273). The half-period for radiotellurium is 139.6 days (Greinacher and Herrmann, Jahrb. Radioaktiv. Elektronik. 1905, 2, 136).

Owing to the minute quantities of polonium available it has been extremely difficult to detect helium as one of its disintegration products, but Curie and Debierne (Compt. rend. 1910, 150, 386) have obtained 1.3 c.mm. of helium from approximately 0.1 mgm. of polonium (cf. Kernbaum, Zeitsch. physikal. Chem. 1907, 8, 339). The spectrum lines  $\lambda = 4642, 4170.5, 3913.6, 3652.1$  probably belong to polonium preparations slowly (Compt. rend. 1909, 148, 1665).

Polonium has been identified with radium F, the last of the series of transformation products of radium that has been recognised. The change from radium to radium F involves the loss of four  $\alpha$  particles from the atom. The atomic weight of polonium should therefore be about 210. The unknown radium G, into which polonium disintegrates, is devoid of sensible radioactivity, since the half period of polonium preparations that have been kept for five years is practically identical with the figure given above (Waters, Phil. Mag. 1910, [vi.] 19, 905). Radium G will probably prove to be lead.

The *radio-lead* of Hofmann and Strauss (Ber. 1901, 34, 3033; Hofmann and Wolff, *ibid.* 1903, 36, 1040) has been shown to owe its activity to the presence of the transformation products *radium D, E and F*. The substance  *$\beta$ -polonium*, described by Giesel (Ber. 1906, 39, 780) was shown later to be radium E (Giesel, *ibid.* 1906, 39, 1014).

**POLYBASITE.** A sulphantimonite of silver (60–72 p.c.) and copper (3–15 p.c.) with the formula  $8(\text{Ag,Cu})_2\text{S}(\text{Sb,As})_2\text{S}_4$  (F. R. Van Horn, Amer. J. Sci. 1911, 32, 40). The antimony may be partly or wholly replaced by arsenic, forming a passage to the isomorphous species *pearceite*: small amounts of zinc and iron are also often present. Both minerals occur as iron-black, six-sided plates with monoclinic symmetry. They are found in the silver-mining districts of Mexico, Colorado, Nevada, &c., sometimes in sufficient abundance to be of importance as ores of silver. L. J. S.

**POLYCHREST SALT.** An old name for normal potassium sulphate; applied also sometimes to Rochelle salt.

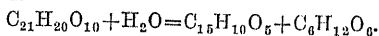
**POLYCHROMINE v. PRIMULINE AND ITS DERIVATIVES.**

**POLYGALIC ACID v. SENEGA.**

**POLYGONIN v. GLUCOSIDES.**

**POLYGONUM CUSPIDATUM.** *P. cuspidatum* (Sieb. et Zucc.), is common in India, China, and Japan, and is referred to by A. Henry in a paper entitled 'Chinese Names of Plants' (Journal Royal China Branch of Royal Asiatic Society, 22, New Series, No. 5, 1887) as 'Kan-yen, wu-tzu,' the name at Peking for the root of the *P. cuspidatum*, which is said to be used for dyeing yellow.

According to Perkin (Chem. Soc. Trans. 1895, 67, 1084), the main constituent of this root is a glucoside *polygonin*  $\text{C}_{21}\text{H}_{36}\text{O}_{10}$ , forming orange-yellow needles, m.p. 202°–203°, which, when hydrolysed by acids, gives *emodin* and a sugar.



A trace of a second glucoside is also present, from which the *emodin monomethyl ether*, m.p. 200°, previously found to exist in the root bark of the *Ventilago madraspatana* (Gaertn.) (Chem. Soc. Trans. 1894, 65, 932) was obtained.

A. G. P.

**POLYHALITE.** A triple sulphate,  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , occurring in some abundance in salt deposits with rock-salt, anhydrite, and gypsum; and it is also found with these minerals in the salt

mines of Ischl, Ebensee, Aussee, Hallstatt, and Hallein in Austria, Berchtesgaden in Bavaria, Vic in Lorraine, and Varangéville near Nancy. The mineral occurs as nodules with a fibrous or platy structure and a brick-red colour, this colour being due to the enclosure of iron hydroxide. On the artificial production of polyhalite, v. J. H. van't Hoff, Sitz. Akad. Wiss. Berlin, 1906, 412 (v. POTASSIUM).

L. J. S.

# **POLYMERISED OILS v. OILS, FIXED, AND FATS.**

**POMEGRANATE**, *Punica granatum* (Linn.). The fruit is edible. It consists of a hard and thick rind, filled with numerous seeds. König gives, : of the pulp—

Water	Protein	Invert sugar	Cane sugar	Other N-free ext.	Acid	Fibre and seed	Ash
79.3	1.2	11.0	0.7	3.8	0.8	2.8	0.5

Analyses of the juice of pomegranates by Bornträger and Paris (Bied. Zentr. 1899, 28, 198) show that in ripe fruit, the juice contains from 0.37 to 0.51 grm. of acid and from 10.5 to 13.69 grms. of reducing sugar per 100 c.c.; in unripe fruit the free acid amounted to from 3.0 to 3.4 grms., the reducing sugar to from 7.8 to 11.3 grms. The must easily ferments and yields a wine with the flavour of raspberries, containing from 4.4 to 7.0 grms. of alcohol per 100 c.c.

The bark of the stem and roots is used in medicine as an astringent and anthelmintic. The root bark is the richer in the active principles—the alkaloids—*pelletierine*, *isopelletierine*, *pseudo-pelletierine* and *methyl-pelletierine*. The first two, constituting usually from 40 to 50 p.c. of the total alkaloids present, are of value as vermifuges: the last two have little or no effect.

The total amount of alkaloids in the bark of the roots grown in the south of France is about 0.6–0.7 p.c., while in the bark of the branches about 0.5 p.c. is present (Ewers, Arch. Pharm. 1899, 237, 49). In the products from Java, the figures were higher (Beckurts, *ibid.* 1900, 238, 8). The alkaloids were first obtained by Tanret (Compt. rend. 1878, 86, 1270) who found pelletierine  $C_8H_{15}NO$  to be a colourless liquid, boiling (with decomp.) at 195°, with a sp.gr. of 0.988, soluble in 20 times its vol. of water: its salts are laevorotatory.

*iso*-Pelletierine is also a liquid of similar composition but is optically inactive; *pseudo*-pelletierine  $C_9H_{15}NO$  is a crystalline solid, methyl-pelletierine  $C_{10}H_{17}NO$  is a liquid boiling at 215°, soluble in 25 parts of water and yielding salts which are very deliquescent.

The alkaloids of pomegranate bark have been studied by Ciamician and Silber (Ber. 1892, 25, 1601; *ibid.* 26, 156; 26, 2738; 1894, 27, 2850); Piccini (Gazz. chim. ital. 1899, i. 408; ii. 311), and Willstätter and Veraguth (Ber. 1905, 38, 1984). The rind of the fruit contains a yellow colouring matter, called ellagic acid (A. G. Perkin, *ibid.* 1897, 71, 1137).

H. I.

## **POMEGRANATE RIND v. TANNINS.**

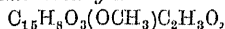
## **PONCEAU v. AZO-COLOURING MATTERS.**

## **PONCEAU CRYSTAL v. AZO-COLOURING MATTERS.**

**POPLAR BUDS.** *Chrysin*  $C_{15}H_{10}O_4$  is contained in the leaf buds of the poplar (*Populus pyramidalis* (Salisb.), *P. nigra* (Linn.), *P. monilifera* (Ait.)), in which it is present to the extent of about  $\frac{1}{2}$  p.c. It was first isolated by Piccard (Ber. 6, 884, 1160; 7, 888; 10, 176) and is best prepared by the method devised by this chemist.

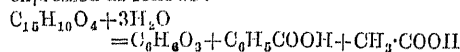
An alcoholic extract of 1000 grams of poplar buds is treated while hot with about 120 grams of lead acetate, and after standing for some time the yellow precipitate is removed. Through the clear filtrate sulphuretted hydrogen is passed in order to decompose lead salts, the sulphide of lead is filtered off and the liquid evaporated to dryness. The residue dissolved in a little hot alcohol gradually deposits crystals of chrysin, which are collected, successively extracted with carbon disulphide, benzene, and boiling water, and finally crystallised two or three times from alcohol.

Pure chrysin crystallises in colourless leaflets, m.p. 275°, and dissolves in alkaline solutions with an intense yellow colouration. When acetylated, *diacetylchrysin*  $C_{15}H_8O_4(C_2H_3O)_2$ , colourless needles, m.p. 185°, is produced, but by the action of acetic anhydride in the usual manner a *monoacetylchrysin*  $C_{15}H_9O_5$ , m.p. 163°, only can be prepared. The latter yields *acetylchrysinmonomethyl ether*

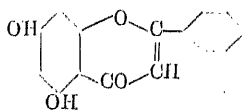


colourless needles, m.p. 149°, and with alcoholic soda gives a bright yellow sodium salt which is decomposed by washing with water (v. Kostanecki, Ber. 1893, 26, 2901).

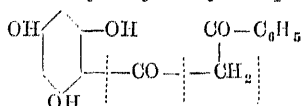
When digested with boiling concentrated potassium hydroxide solution, chrysin gives *phloroglucinol*, *benzoic acid*, *acetic acid* and *acetophenone* (Piccard, *l.c.*), the last-named in very small quantity and the reaction can be expressed as follows:



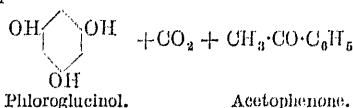
An investigation by Kostanecki (*l.c.*) indicates that chrysin is a *dihydroxyflavone* and possesses the constitution



The first hypothetical product of the hydrolysis of chrysin by means of alkali (compare flavone) is 2:4:6-trihydroxybenzoylacetophenone

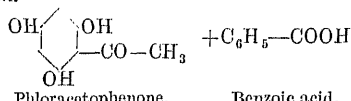


which subsequently yields *phloroglucinol* and *acetophenone* and carbon dioxide

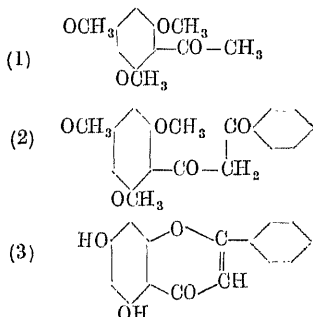


On the other hand, *phloroacetophenone* (which is unstable in the presence of alkali and is therefore converted into phloroglucinol and acetic

acid) and benzoic acid may also be produced.



Chrysin has been synthesised by Emiliewicz, v. Kostanecki and Tambor (Ber. 32, 2448) in the following manner.



The latter, when digested with strong boiling hydriodic acid, is demethylated and ring formation occurs with the production of chrysin (3).

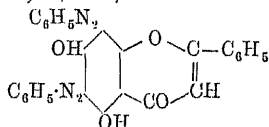
The following derivatives of chrysin have been prepared.

*Dibromchrysin*  $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_4$  (Piccard, Ber. 1873, 6, 886); *Di-iodochrysin*  $\text{C}_{15}\text{H}_8\text{I}_2\text{O}_4$ , yellow needles (Piccard); *Chrysinmonoethylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_2\text{H}_5)$ , red leaflets, m.p. 21°.

*Chrysinmonoethylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_2\text{H}_5)$ , thin needles (m.p. 146°) (Piccard); *Chrysinisomylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_5\text{H}_{11})$ , thin needles, m.p. 125° (Piccard); *Dibromchrysinisomylether*  $\text{C}_{15}\text{H}_7\text{Br}_2\text{O}_3(\text{OC}_5\text{H}_{11})$ , needles, and *dinitro-diacytylchrysin*  $\text{C}_{15}\text{H}_6\text{O}_4(\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O})_2$ , yellow needles, m.p. 229° (Darier, l.c.).

*Chrysinmonoethylether* (Perkin, Chem. Soc. Tra. 1894, 27, 21); *Chrysinmonoethylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_2\text{H}_5)$ , thin needles (m.p. 146°) (Piccard); *Chrysinisomylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_5\text{H}_{11})$ , thin needles, m.p. 125° (Piccard); *Dibromchrysinisomylether*  $\text{C}_{15}\text{H}_7\text{Br}_2\text{O}_3(\text{OC}_5\text{H}_{11})$ , needles, and *dinitro-diacytylchrysin*  $\text{C}_{15}\text{H}_6\text{O}_4(\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O})_2$ , yellow needles, m.p. 229° (Darier, l.c.).

*Chrysinmonoethylether* (Perkin, Chem. Soc. Tra. 1894, 27, 21); *Chrysinmonoethylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_2\text{H}_5)$ , thin needles (m.p. 146°) (Piccard); *Chrysinisomylether*  $\text{C}_{15}\text{H}_9\text{O}_3(\text{OC}_5\text{H}_{11})$ , thin needles, m.p. 125° (Piccard); *Dibromchrysinisomylether*  $\text{C}_{15}\text{H}_7\text{Br}_2\text{O}_3(\text{OC}_5\text{H}_{11})$ , needles, and *dinitro-diacytylchrysin*  $\text{C}_{15}\text{H}_6\text{O}_4(\text{NO}_2)_2(\text{C}_2\text{H}_3\text{O})_2$ , yellow needles, m.p. 229° (Darier, l.c.).



orange-red needles, m.p. 251°–252°, insoluble in alkaline solutions, is unaltered by prolonged digestion with acetic anhydride.

Chrysin is a feeble dyestuff. The shades produced on wool mordanted with aluminium, chromium and iron, are respectively pale bright yellow, pale yellow-orange, and chocolate brown.

*Tectochrysin*, a second constituent of poplar buds, is present in the benzene extracts from the crude chrysin. *Tectochrysin* is chrysin monomethylether ( $\text{C}_{15}\text{H}_9\text{O}_3\text{OCH}_3$ ) (Piccard), and is identical with the methylation product of chrysin itself.

**POPPY SEED OIL.** Poppy seed oil is obtained from the seeds of the two varieties of

poppy, *Papaver somniferum* (Linn.), viz. *P. album* and *P. nigrum* (DC.), by pressing. The plant is grown extensively in Asia Minor, Persia, India, Egypt, South Russia, and the North of France. The seeds yield from 45–50 p.c. of oil. The seed produced in Manchuria is grown together with other wild seeds yielding about 16 p.c. of a non-drying oil; hence the Manchurian oil is of very low quality as regards drying powers.

In France a distinction is made between *huile d'œillette* and *huile de pavot*. The former is obtained from indigenous, or at any rate European, poppy seed, whilst the name *huile de pavot* is given to the oil obtained from oversea seed. Since by far the greatest part of expressed oils, both of European as also of oversea origin, is used as a table oil, all edible poppy seed oils are termed *huile d'œillette*.

The 'cold drawn' oil, the oil of the first expression, is almost colourless or very pale golden yellow; this is the 'white poppy seed oil' of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the 'red poppy seed oil' of commerce.

'Sweet' (fine) table oils prepared by cold expression in Marseilles and in the north of France (in Lille, Arras, Douay, Cambrai). The cold-pressed oil is filtered before being placed on the market. In some of these establishments paper filters are said to be used even at present.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

The cakes resulting as a by-product are rich in nitrogen and are fed to cattle; only when the cakes have become mouldy are they employed as a manure for early fruit.

For the chemical and physical characteristics, see tables under OILS, FIXED, AND FATS.

Poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually expressed in the same works in which sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil and also with hazelnut oil to improve the taste of the edible oil obtained from stored seeds.

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the bromide test (see OILS, FIXED, AND FATS). Walnut oil yields from 1.4 to 1.9 p.c. of ether-insoluble brominated glycerides, whereas poppy seed oil yields none.

**POPULIN** (*Benzoyl salicin*)  $\text{C}_{20}\text{H}_{22}\text{O}_8 \cdot 2\text{H}_2\text{O}$  is a glucoside contained in the bark and leaves of the Poplar, *Populus tremula* (Linn.), from which it is extracted by boiling the leaves with water. The extract is precipitated with lead acetate and the filtrate is treated with sulphuretted hydrogen, after which it is decolourised with charcoal, evaporated and recrystallised (Piccard, Ber. 1873, 6, 890; Hallwachs, Annalen, 1857, 101, 372; Piria, *ibid.* 1855, 96, 376). It can be readily obtained also by the following process.

A solution of 20 grams of salicin in a litre of

water is rendered alkaline with potassium hydroxide and 10 grams benzoyl chloride are added very slowly with constant stirring, more alkali being added from time to time so as to avoid the formation of much free acid. The populin separates as a bulky white precipitate, which is dried, powdered, and extracted with ether. The insoluble residue is recrystallised from boiling water and subsequently from hot alcohol (Dobbin and White, Pharm. J. 1904, 73, 233).

It forms colourless prismatic needles which lose their water of crystallisation at  $100^{\circ}$ , and melt at  $180^{\circ}$ . It has a sweetish somewhat acid taste, is laevorotatory (Biot and Pasteur, J. 1852, 179), is sparingly soluble in ether and in cold water but readily so in hot water and in alcohol.

When boiled with lime or baryta water it is decomposed into salicin and benzoic acid. With nitric acid it yields *benzohelicin*  $C_{20}H_{20}O_8$ , and in strong sulphuric acid it dissolves with a red colour. When boiled with dilute acids it yields *saliretin*, benzoic acid and glycoze (Lippmann, Ber. 1879, 12, 1649). V. GLUCOSIDES.

**PORCELAIN** v. POTTERY.

**PORCELAIN CLAY** v. CLAY.

**PORCELAIN STONE** v. CLAY.

**PORPEZITE**. A native alloy of gold and palladium.

**PORPHYRY**. A term loosely applied to any rock in which distinct crystals are embedded in a fine-grained ground-mass. The structure is well seen in many igneous rocks, where crystals have consolidated from a molten magma before the eruption of the mass. The typical porphyry of the ancients, *lapis purpureus*, contains crystals of white or pink felspar in a purple, crimson, or chocolate-coloured base, whence the original name *πορφύρεος* or *πορφύρεως λίθος*. It was extensively quarried by the Romans at Jebel Dokhan ('Mountain of Smoke'), in eastern Egypt, and is described by Latin writers as *lapis purpureus*; but although regarded as the most sumptuous of decorative stones, and largely used by Roman architects and sculptors for pillars, pavements, busts, and sarcophagi, it appears to have been unworked by the ancient Egyptians.

The crystals in the ancient red porphyry were analysed by Delesse, who found them to be a lime-soda plagioclase (Bul. Soc. Géol. France, 2 sér. 7, 484). The crypto-crystalline ground-mass contains much felspar altered to a reddish manganiferous epidote (withamite). The red colour of the rock is mainly due to the large quantity of finely divided hæmatite (J. Couyat, Compt. rend. 1908, 147, 988). Beautiful crystals of hornblende occur in the ancient red porphyry, and the rock may be described as a *hornblende-porphyr*. The history of the rock has been fully worked out by O. Schneider (Ueber den roten Porphy der Alten, Dresden, 1887). The Egyptian quarries have been visited and described by Williamson and other travellers (v. W. Brindley, Trans. R. Inst. Brit. Architects, 1888). Red porphyry, somewhat similar to the Egyptian, but less beautiful, occurs in the Sinaitic peninsula, at Elfdalen in Sweden, and in Siberia. The *porfido rosso antico* of Egypt is to be clearly distinguished from *rosso antico*, or the ancient red marble of Laconia.

The green porphyry of the ancients (*porfido verde antico*), known to Italian antiquaries as *serpentino*, was worked at Mount Taygetus in the Morea, and termed *lapis Lacedæmonius*. It contains white, or pale-green, crystals of plagioclase, embedded in a ground-mass filled with viridite, or chloritic products of the alteration of ferro-magnesian silicates. A similar, but less handsome, stone is the *porphyry* of Lambay Island, near Dublin. Of Cumberland also yields a similar rock.

The *quartz-porphyr*ies, belonging to the acid group of igneous rocks, and known in Cornwall as *elvans*, contain well-developed crystals of quartz, and often also of felspar, embedded in a felsitic ground-mass, consisting of a minutely crystalline aggregate of felspar and quartz. The elvans are sometimes worked as ornamental stones. Many granite rocks are beautifully porphyritic, and some of the Cornish granites owe their character to the presence of bold crystals of orthoclase. Fine crystals of pink and salmon-coloured orthoclase form the characteristic feature of the well-known porphyritic granite of Shap in Westmoreland, and of the handsome luxullianite of Cornwall. F. W. R.

**PORPOISE OIL**. Porpoise oil is obtained from the brown porpoise, *Delphinus phocaena* (Linn.). The oil from the blubber is kept separate from that prepared from the cavities in the head and from the jaw, exactly as in the case of dolphin oil (see OILS, FIXED, AND FATS tables). Hence we differentiate between *body oil* and *jaw oil*.

Both oils are characterised by the high proportion of volatile fatty acids they yield on saponification. The jaw oil contains much higher proportions of volatile acids than does the body oil. The oil is used, like dolphin oil, for lubricating delicate machinery, especially type-writing machines. J. L.

**PORTLAND CEMENT** v. CEMENTS.

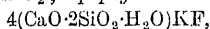
**PORTUGALLO OIL**. Essential oil of orange peel (v. OILS, ESSENTIAL).

**POTASSIUM**. Symbol K. At.w. 39.1.

*Occurrence*. Potassium occurs, principally as chloride and sulphate, in sea-water and other natural waters, a litre of the former containing from 0.5 to 0.7 gram of the element. As chloride or carbonate, or as an organic salt, it occurs in soils and vegetable and animal substances. Thus, wood ashes contain much potassium carbonate, which also forms a considerable proportion of the ash of marine plants, such as *laminaria* and *fuci*. Potassium occurs as *sybrite* or *sybrite* KCl, and as *carminite* KCl-Mg(Cl<sub>2</sub>, 6H<sub>2</sub>O), especially in the beds overlaying the great salt deposits of Stassfurt. As nitrate, it is found as an efflorescence on the soil, usually together with the sodium salt, in Peru, Chile, &c., and as

in many mineral waters, such as Vichy. As the double sulphate of aluminium and potassium, it occurs in *alumstone* or *alunite*  $3Al_2SO_4 \cdot K_2SO_4 \cdot 6H_2O$ , principally in trachyte and other rocks subjected to the action of sulphurous gases. It is found as bitartrate in wines, and as sulphate, carbonate, and chloride in beetroot molasses. As an organic salt (sudorate), it occurs in the 'suint' of sheep, and is separated therefrom as carbonate together with wool fat (Langbeek, J. Soc. Chem. Ind. 1890, 356).

The main source of potassium, however, is the primitive rocks, in which it occurs as *orthoclase* (potash felspar)  $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$ ; *muscovite* (potash mica)  $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ; *leucite*  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ; *apophyllite*



and other zeolites, and in many other silicates.

The sources from which potassium salts are obtained for technical purposes are—firstly, the sea-water; secondly, the mineral crust of the earth; thirdly, the vegetable, and to some extent the animal, kingdom.

The quantity of potassium salts contained in sea-water is not very large, but it has been found economically possible to extract it therefrom, as we shall see in the case of potassium chloride. Indirectly, the potassium salts obtained in the working up of kelp are derived from this source.

The mineral crust of the earth contains about 2.4 p.c.  $\text{K}_2\text{O}$  in the state of *silicates*, as a constituent of several of the most important minerals as felspar and mica; hence both older and younger rocks (granite, mica, slate, basalt, &c.) are sources of potash. By the decay of the rocks containing these minerals, potassium compounds have been spread all over the earth as part of the arable soil; from this source are derived, not only the potassium compounds contained in all plants, but probably most of those contained in sea-water. The importance of this occurrence of potash is enormous for the existence of all organisms; but it has not been possible so far to extract potassium compounds for technical purposes from the natural silicates or the arable soil in an economical way.

Several other salts of potassium are, however, more adapted for this purpose. Potassium *nitrate*, as found in the crude state, especially in India, is certainly more valuable in respect of its acid than of its alkaline constituent; but the latter is also very important. The best proved by the large quantity of potassium chloride employed for the artificial saltpetre.

Potassium sulphate occurs in large quantities in alum rock, and in several of the minerals found together with carnallite in the Stassfurt deposits.

Potassium chloride is found both in the pure state, as *sylvestine*, and in much larger quantities as *carnallite*, in the Stassfurt deposits and some other places. This is at present the most important of all the sources from which potassium salts are obtained for technical purposes.

In the vegetable kingdom potassium is universally found, principally in the contents of the cells and vessels, and in the organic acids. It is found in the ashes as carbonates, chlorides, or less sulphate, chloride, &c.

It is unnecessary to say that all this potassium is derived from the soil on which the plants grow; but for many centuries, indeed, apart from saltpetre and kelp, nearly up to the middle of this century, wood ashes formed practically the only source of potassium compounds employed for technical purposes. Another important source of potassium salts is the ashes of seaweeds, called *kelp* in Scotland and *varec* in Normandy, which from times immemorial have been obtained by

employing the seaweed as fuel; since 1811, when iodine was discovered in these ashes, and a special industry had been founded thereon, those potassium salts have also been utilised. Somewhat later another vegetable source was opened out for potassium compounds—viz. the *vinasse*—that is, the residue left on distilling fermented beet-root molasses. Hence the expression 'vegetable alkali,' by which it is distinguished from soda, when it is used, had proved the separate existence of those bodies, was altogether appropriate, not only at this time, but even much later, until the Stassfurt discoveries made that designation altogether unsuitable.

Even the animal kingdom contributes a certain quantity of potassium compounds, in the shape of the carbonate of potash from the 'yolk' of sheep's wool (*suint*).

Interesting communications on the history of potashes are made by E. O. von Lippmann in Chem. Zeit. 1908, 977.

**Metallic potassium.** The compound nature of the alkalis, and the presence in them of oxygen, had been suspected previous to 1807 (*v. Lavoisier, Traité de Chimie*, II. 194), but the isolation of potassium was not effected until that year, when Davy obtained it by electrolysis of the fused hydroxide (*Phil. Trans.* 1808, 1; 1809, 39; and 1810, 16). The metal was soon prepared in larger quantity by Gay-Lussac and Thénard (*Ann. Chim. Phys.* 1808, 65, 325, and 1808, 66, 205) by slowly passing the hydroxide over iron filings heated to whiteness in a gun-barrel protected by a luting of clay, their process being modified by Berzelius (*Gilbert's Annalen*, 6, (N. F.) 198), Mantell (*Annals of Philosophy*, Thompson and Phillips, 22, 232), Gmelin (*Handb.* 3, 5), and Tennant (*Annalen*, 93, 291).

An important improvement was next introduced by Curandau (*Ann. Chim. Phys.* 1808, 66, 97, and *Phil. Mag.* 1810, 36, 283), who replaced the iron by carbon or carbonaceous matter. This, and the other processes in use, were examined by Brunner (*Bibliothèque Universelle de Genève*, 1823, 22, 36, and Schweigger's *J. für Chem. und Phys.* 35, 517), who also improved upon the apparatus used by Scholtz (*Ann. Chim. Phys.* 73, 333) and Gilbert's (*Annalen*, 30, 333), Lampadius (*Schweigger's J. für Chem. und Phys.* 34, 221), and others.

Brunner's process as improved by Wöhler (*Pogg. Ann.* 1825, 4, 23, and 474), consists in carbonising potassium bitartrate in a covered vessel, the bottom of which is lined with carbon and covered with a layer of charcoal, and the vessel is placed in a powerful wind furnace. Kukla (*Zeitsch. für Phys. und verwandte Wissenschaften*, 1837, 5, 466), Werner (*J. pr. Chem.* 14, 267), Schöedler (*Annalen*, 20, 2), and Gale (*Amer. J. Sci.* 19, 205, and 21, 60), proposed various arrangements and lutes for protecting the retort from the furnace, the two first, and Fleischl (*Zeitsch. für Phys. und verwandte Wissenschaften*, 2, 307 and 343, 3, 326) also proposing modifications in the mixture used.

The method of condensing was next improved by Donny and Mareska (*Ann. Chim. Phys.* [iii.] 35, 147, *v. also* Mitscherlich, *Lehrb. der Chem.* 2, 10); while the addition of chalk to the mixture was found to facilitate the reduction

by rendering the mass pasty instead of liquid at the reduction temperature, thus preventing the separation of the carbon from the alkali (*v. Deville, De l'Aluminium (Paris, 1859), 650; and Kühnemann, J. 1864, 180*).

For the preparation of potassium in a state of greater purity, Matthiessen (*Chem. Soc. Trans. 1855, 8, 27*) proposed the electrolysis of the easily fusible mixture of potassium and calcium chlorides.

The use of sodium instead of potassium for the manufacture of aluminium was introduced in 1854 by Deville (*Ann. Chim. Phys. 1856, 46, 415*), who also made improvements in the manufacture of the metal. Since then, sodium has almost entirely replaced potassium for use in the arts. The inconvenience and waste attending the manufacture of potassium, owing to the production of explosive compounds with carbon monoxide (*v. Liebig, Annalen, 11, 182, and Brodie, Chem. Soc. Trans. 12, 269*), accounted to some extent for its former high price. By Castner's electrolytic process potassium can be produced at a price not greatly exceeding that of sodium.

The various processes employed in the preparation of potassium are identical with those used in sodium manufacture, and are described, together with a list of patents and other matters relating equally to both metals, in the article SODIUM.

Potassium obtained in this way, in which carbon monoxide is a product, evolved gases, always contains the explosive compound above mentioned, which renders it liable to detonate on the slightest friction. For this reason, it must be redistilled, once or twice, when so prepared.

**Properties.**—Potassium, when freshly cut, has a brilliant, silvery metallic lustre. It crystallises in obtuse octahedra, showing a greenish-blue tint (*Long, Chem. Soc. Trans. 1860, 13, 124*).

According to Baumhauer (*Ber. 6, 655*), its sp. gr. at 13° is 0.875. At 0°, potassium is brittle, and possesses a crystalline fracture. At 15°, it acquires a waxy consistency and a few degrees higher becomes pasty, melting at 62.5° (*Bunsen, J. 16, 178*) and boiling at 719°–731° according to Carnelley and Carleton Williams (*Chem. Soc. Trans. 1879, 565*), or at 667° according to Perman (*Chem. Soc. Trans. 1880, 328*). The vapour has a green colour, and attacks glass and porcelain. Its characteristic channelled absorption spectrum has been examined by Roscoe and Schuster (*Proc. Roy. Soc. 22, 362*).

The lowering of the melting-point of potassium by the presence of sodium, gold, and thallium has been determined by Heycock and Neville (*Chem. Soc. Trans. 1889, 666*).

Potassium dissolves in liquefied anhydrous ammonia forming a deep-blue solution, from which the metal is re-obtained on evaporation of the ammonia (*Seeley, Chem. News. 23, 169*). It is the most electro-positive element known with the exceptions of caesium and rubidium, and is an extremely powerful reducing agent. Hence the use of potassium for the preparation of less electro-positive elements, such as boron, silicon, magnesium, aluminium, &c., for the reduction of gases containing oxygen out of organic and other compounds.

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On exposure to the air, it rapidly becomes converted into the hydroxide and finally into the carbonate. It decomposes water with sufficient energy to ignite the liberated hydrogen. Carbon dioxide passed over heated potassium is reduced to carbon, with formation of potassium oxide.

Potassium unites directly with the halogens and with sulphur, selenium, tellurium, and phosphorus, burning brilliantly when heated with them. When heated in carbon monoxide it forms a black mass identical with the explosive body produced in the manufacture of potassium.

**Alloys.** Potassium forms alloys with most metals, usually by being heated with them. The more important alloys are described under the various metals. With sodium, potassium forms alloys of low melting-point, as observed by Davy. Graham and Wanklyn (*Phil. Mag. 3, 21*) obtained an alloy melting below the ordinary temperature and containing about one-fourth its weight of potassium by heating sodium with potassium hydroxide to about 171°; whilst Wanklyn (*Chem. News. 3, 66*) has obtained a similar alloy by heating sodium with potassium acetate.

Potassium combines directly with mercury, with evolution of heat. The melting-points of a number of these amalgams have been determined by Merz and Weith (*Ber. 14, 1445*). When containing 70–96 parts of mercury to 1 part of potassium, the amalgam is crystalline. With 30 parts of mercury, it is hard and brittle. When heated to 440°, they all leave a crystalline residue of the composition  $HgK_2$ , spontaneous on exposure to air (*De Souza, Ber. 14, 1445*). At all the mercury is evolved below a red heat. Kraut and Popp (*Annalen, 159, 188*) have prepared a crystalline amalgam of the composition  $Hg_{10}K_3$ .

**Potassium oxide.**  $K_2O$  is made by the *Badische Anilin- und Soda-Fabrik* (D. R. P. 143216) by heating potassium nitrate with metallic potassium, air being excluded:  $KNO_3 + 5K = 3K_2O + N$ . For the same purpose the nitrite  $KNO_2$  may be employed, and in the same manner mixtures of  $K_2O$  and  $Na_2O$  may be obtained.

**Potassium peroxide,**  $K_2O_2$ , is industrially prepared by Jaubert (D. R. P. 189822) by heating, with special precautions, an alloy of potassium with lead, tin, or sodium at a moderate temperature in a current of air.

**Potassium hydroxide** *v. infra*.

**Potassium chloride.** This salt, which in commerce is generally known as '*muriate of potash*,' was formerly obtained as a by-product in various manufactures, such as the working up of kelp for iodine, from the spent lye of soap-makers, in refining native saltpetre, &c. The quantities thus obtained were not very large, if compared with the present state, and they were principally used in the manufacture of alum and of potassium chlorate. Some more potassium chloride was afterwards obtained in Balard's process of working-up the mother-liquors from the manufacture of sea-salt, and a good deal more in the manufacture of potashes from vinasse (*cf. Potassium carbonate, infra*).

But all this sinks into insignificance beside the enormous quantities obtained from the *Stassfurt carnallite*, and we shall therefore here describe the *Stassfurt* occurrence of potassium.



salts, as well as the methods of manufacture pursued here.<sup>1</sup>

The village of Stassfurt is situated on the river Bode, not far from Magdeburg, in Prussian Saxony, close to the borders of the small principality of Anhalt. In 1850 Stassfurt numbered 2000 inhabitants; in 1885, owing to the development of the carnallite industry, 16,000, and the adjoining newly-formed village of Leopoldshall (in Anhalt), 4000 inhabitants. The Stassfurt brine-springs are mentioned as far back as 1227, and in the last century 7,000 tons of salt per annum were made there in 30 salt-pans; but about 1815 the production of salt from brine was stopped there, having ceased to be remunerative

in the face of competing brine-springs. In 1830 the Prussian mining office commenced boring for rock-salt, and in 1843 the salt was struck at a depth of 850 feet. The boring was continued for another 1080 feet without getting to the bottom of the stratum of salt; but the brine pumped up was extremely impure, containing, together with sodium chloride, a large quantity of magnesium chloride, potassium chloride, and magnesium sulphate. It was, however, conjectured at once that these salts might be deposited in separate strata, and it was resolved to sink two shafts. These were commenced in 1852, and within five years they had reached a thick stratum of pure rock-salt, after having

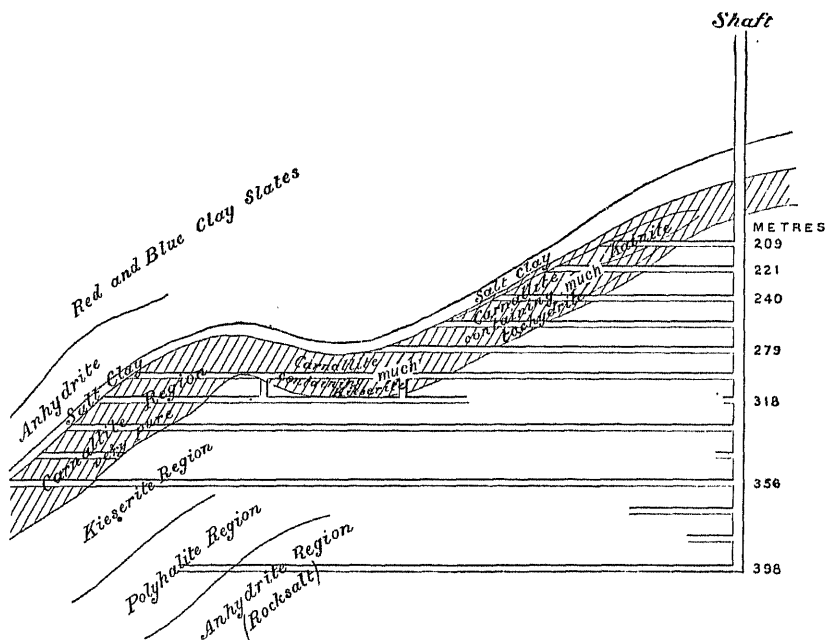


FIG. 1.

penetrated a number of strata of other salts, of an aggregate thickness of 530 feet, which were called 'abraumsalze,' because they were at first considered useless, and had to be taken away before getting to the rock salt.

Later on it was found that the salt deposits occupy an enormous basin in the North German Plain, which has been successfully tapped in several other places, of which we mention only Spereberg, near Berlin, where the boring was continued through the enormous thickness of 3940 feet of salt without getting to the bottom; also at Segeberg, near Lübeck, and in other places. But *potassium* salts in great quantity

until quite recently had been found only in one locality, in the vicinity of Stassfurt, where the 'Abraumsalze' occur in the Upper New Red Sandstone. According to Chem. Zeit., Aug. 22, 1911, large deposits of sylvine have been discovered in Upper Alsace, in an area of about 200 square kilos., near Mülhausen. Two strata have been found, the upper one 3 feet thick, the lower one more than 16 feet thick estimated to contain some 1500 tons, but the borings will have to be deep, say 1600 to 2100 feet, which entails a very high temperature. This field, unlike the North German deposits, seems to be continuous, without faults. Geologically it is much more recent than the Stassfurt beds. But the recovery of potassium salts from the Alsatian field has not yet become a commercial fact, and we therefore confine our description to the Stassfurt deposit:—

In 1856 and 1857, the two Prussian shafts at Stassfurt; in 1861, the Anhalt shaft at Leopoldshall; in 1876, two shafts at Leopoldshall; in 1878-1883, another two shafts at Stassfurt;

<sup>1</sup> To a great extent the detailed description is given in his Handbuch der Kali-Industrie (1908); Krüger, Die Kali-Industrie (1909); Ehrhardt, Die Kali-Industrie (1907); P. 107. A very important series of researches on the formation of the Stassfurt deposits has been made by van't Hoff and his coadjutors, in 1897 and later on.

in 1883, a shaft at Aschersleben, sunk by the Continental Diamond Rock-Paving Company; some more shafts at Vienenburg, at Schönebeck, and at Vienenburg.

The profiles (Figs. 1 and 2) give an idea of the strata pierced in the two oldest and most important shafts at Stassfurt and Leopoldshall.

At Stassfurt itself the total thickness of the salt strata is estimated at about 2500 feet, and the time necessary for their formation at about 8000 years. F. Bischof, who has examined

them most thoroughly, divides them into the four following 'regions,' of which only the first and the last have become of technical importance.

1. *Anhydrite or rock-salt region*, so called from the strings of anhydrous calcium sulphate which divide the rock-salt into bands of an average thickness of nearly 4 inches, each of which is supposed to be a year's growth. The layers of calcium sulphate are only  $\frac{1}{4}$  inch thick, and amount only to 4 p.c. by weight of the rock-salt in the upper strata, or 9 p.c. in the lower strata.

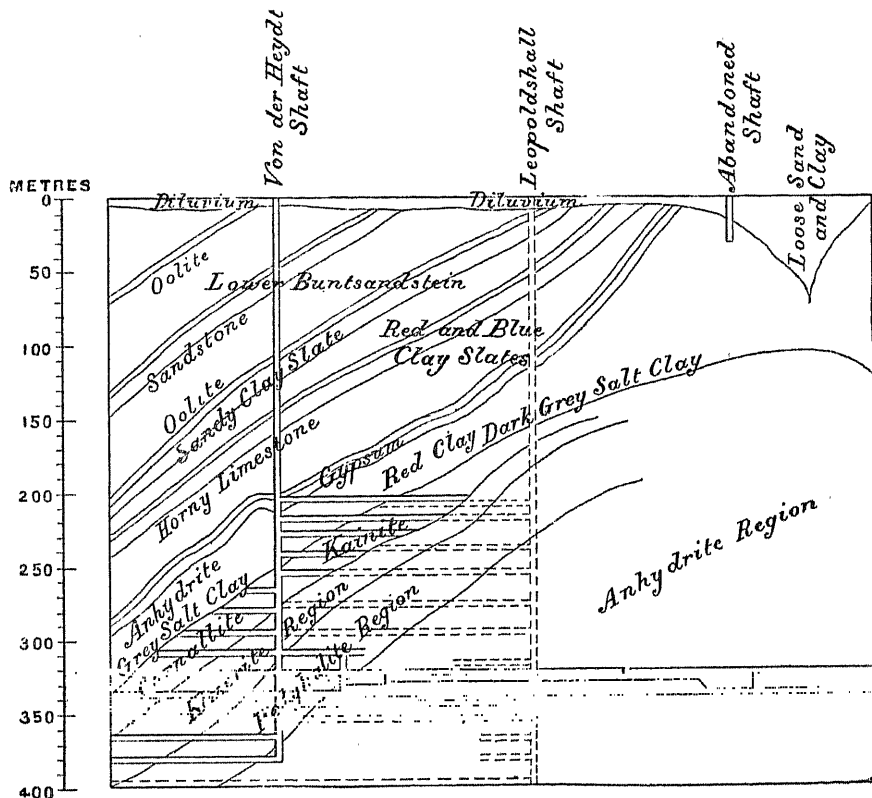
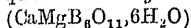


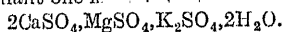
FIG. 2.

By mechanically separating the anhydrite, rock-salt of 99 p.c. NaCl can be obtained on a large scale. Small quantities of *hydroboracite*



and of a strontium sulphate are found here as well. The thickness of this stratum varies a great deal; in the centre of the basin it may be estimated at about 2000 feet.

2. *Polyhalite region*. Here the rock-salt is already mixed with polyhalite, of which the dominant one is



Magnesium chloride accompanies the rock-salt, and small quantities of sulphur and of bituminous substances are found here. The average composition of this stratum is: 91 rock-salt,  $6\frac{1}{2}$  polyhalite,  $\frac{1}{2}$  anhydrite,  $1\frac{1}{2}$  magnesium chloride; its thickness is 207 feet.

3. *Kieserite region*, so called from the occur-

rence of white bands of *kieserite*  $\text{MgSO}_4, \text{H}_2\text{O}$ . The average mixture is:

- 65 p.c. rock-salt
- 17 " *kieserite*
- 13 " *carnallite*
- 3 " *bischofite*,  $\text{MgCl}_2, 6\text{H}_2\text{O}$
- 2 " *anhydrite*.

This stratum has a thickness of 187 feet.

4. *Carnallite region*. This contains 55 p.c. of *carnallite*  $\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$ , the most valuable of the Stassfurt salts, together with 25 p.c. rock-salt, 16 p.c. *kieserite*, the remaining 4 p.c. consisting of magnesium chloride (*bischofite*)  $\text{MgCl}_2, 6\text{H}_2\text{O}$ , magnesium bromide  $\text{MgBr}_2, 6\text{H}_2\text{O}$ , *tachydrite*  $(\text{CaCl}_2, 2\text{MgCl}_2, 12\text{H}_2\text{O})$ , *boracite* or  $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$ , *anhydrite*  $\text{CaSO}_4$ , *reichertite*  $(\text{CaSO}_4, \text{MgSO}_4, \text{K}_2\text{SO}_4)$ , clay, sand, micaceous substances. The thickness of this stratum is 140 feet.

In some places the action of water has produced important changes in this region which have replaced the kieserite and part of the carnallite by *kainite*  $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$ ; or  $KCl \cdot MgSO_4 \cdot 3H_2O$ , according to another way of grouping the constituents (about 55 p.c. of the whole), part of which has passed over into *schoenite* (*picromerite*)  $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ . In other places the magnesium chloride has been washed out entirely, and the mixture contains 20 p.c. of pure potassium chloride, *sylvine*, with 30 to 40 p.c. of rock-salt, and an equal quantity of kieserite and other impurities. Only exceptionally *astrakanite*  $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$  is found.

Other Stassfurt minerals of minor importance are: *leonite*  $K_2Mg(SO_4)_2 \cdot 4H_2O$ ;

*Wweite*  $K_2Mg(SO_4)_2 \cdot 2\frac{1}{2}H_2O$ ;

*langbeinite*  $K_2Mg_2(SO_4)_3$ ; *glaserite*  $K_3Na(SO_4)_2$ ;

*vanthoffite*  $Na_6Mg(SO_4)_4$ ;

*krugite*  $K_2MgCa_4(SO_4)_3 \cdot 2H_2O$ ;

*pinnoite*  $MgB_2O_4 \cdot 3H_2O$ ;

*ascharite*  $Mg_6B_6O_{18} \cdot 2H_2O$ ;

*kaliborite* or *heinzite*  $KMg_2B_2O_7 \cdot 2H_2O$ ;

*nesium sulphoborite*  $Na_2Mg_2B_2O_7 \cdot 2H_2O$ .

The salts are cov of salt-clay, over this from 133 to 300 feet of *anhydrite*, and this again by 80 to 100 feet of very pure, transparent *rock-salt*, free from calcium sulphate, evidently a secondary formation.

**Formation of the Stassfurt deposits.** There can be no doubt that the formation of the salt deposits of the North German Plain has been caused by the evaporation of sea-water. But there must have been special causes why, in a comparatively small part of that large area—viz. in the vicinity of Stassfurt—potassium and magnesium salts have been separated in large quantities, whilst on the greatest part of the ground only rock-salt and anhydrite are found.

According to Regnault, the average composition of sea-water is:

Total percentage of solids . . . 3.53  
consisting of:

Sodium chloride . . .	76.49
Potassium chloride . . .	1.98
Magnesium chloride . . .	10.20
Magnesium bromide . . .	0.06
Calcium chloride . . .	6.51
Calcium bicarbonate . . .	3.97
	0.08

99.29

We find here all the materials for the formation of the Stassfurt deposits, the average composition of which has been stated by Bischof, as follows:

	Percentage expressed in minerals
Rock-salt . . .	85.1
Anhydrite . . .	5.7
Polyhalite . . .	0.8
Kieserite . . .	3.3
Carnallite . . .	6.2
Magnesium chloride . . .	0.9

Percentage expressed in salts

Sodium chloride . . .	85.9
Potassium chloride . . .	1.7
Potassium sulphate . . .	0.2
Magnesium chloride . . .	2.6
Magnesium sulphate . . .	3.1
Calcium sulphate . . .	4.0
Chemically-combined water . . .	3.3

Since Bischof's time the bottom of the deposit has been reached, and it can now be said that the percentage of sodium chloride and of calcium sulphate is much higher than he assumed.

If we compare the composition of the Stassfurt deposits with the results of the artificial evaporation of sea-water as carried out in 1849 by Usiglio (Ann. Chim. Phys. [iii.] 27, 92), we find that there are some differences, partly caused by the long duration of the natural process and its yearly interruption, partly by the loss of mother-liquor (*v. infra*). The various salts were transformed into the minerals now present by a subsequent loss of water and by their mutual interaction. The composition of those minerals is, however, not the same as that of the sea-water, caused by the

autumnal influx of fresh sea-water. One remarkable difference also is this: whilst in artificial evaporation the calcium sulphate is entirely precipitated at an early stage, it is formed at Stassfurt even in the strata consisting of mother-liquor salts. Why the calcium sulphate at Stassfurt is in the form of anhydrite, not in that of gypsum ( $CaSO_4 \cdot 2H_2O$ ), as in the artificial evaporation of sea-water, we understand now from the observations of Hoppe-Seyler (Chem. Zentr. 1866, 217) and Rose (*ibid.* 1871, 613), according to which the hydration water of gypsum is abstracted from it by contact with a nearly-saturated solution of sodium chloride, a condition which we must assume to have existed at Stassfurt.

It is quite evident that the Stassfurt deposits have not been formed by the simple evaporation of a basin of normal sea-water, which would have been required to possess a depth of about 30 miles, and which would have produced a very different arrangement of salts. There must have been conditions similar to those even now found present in some of the Sarmatian lakes. Thus Göbel found at the bottom of Lake Elton a salt deposit of a thickness of 12 feet, consisting of 100 annual layers, which increased

lake is filled with a saturated brine; by the surface-evaporation in summer, crusts of common salt are formed, which sink to the bottom. Later on, the common salt gets mixed with Epsom salt and other mother-liquor salts, which form a porous, bitter, and deliquescent layer. The autumnal rains and floods partly dissolve and partly densify this top layer, and at the same time cover it with black mud, thus forming a distinct boundary line upon which the next year's crusts are formed again. In spring the water of that lake contains 13.5 p.c. sodium chloride and 10.5 p.c. of magnesium chloride; in autumn it holds but a small quantity of liquor containing only 4 p.c. NaCl, with 20 p.c.  $MgCl_2$ .

The nearest approach to the Stassfurt condition is found in the Adji-Darja Bay, in the east of the Caspian Sea, a bay of a superficial area of 2000 or 3000 sea miles, and almost entirely separated from the Caspian by a bar. There is, however, a small channel through which the water, abstracted by the intense evaporation within the bay, is replenished from the Caspian. This causes a continuous separation of salt, which is estimated by Schleiden at about 400,000 tons per diem, and the formation of a mother-liquor, part of which finds its way back into the Caspian. Where the depth of the bay is greater, the concentrated liquor sinks to the bottom, causing a state of sursaturation at this place and the deposition of mother-liquor salts. Without this, practically all the mother-liquor would flow back over the bar, and no mother-liquor salts would be formed; and this seems to have been the condition of most of the rock-salt, forming basins of former geological periods. In the case of the Stassfurt salts we must undoubtedly assume an *intermittent* influx of water, and also a number of geological elevations and depressions of level in order to account for the succession of the various strata. We may, with very great probability, assume the following play of causes: the Stassfurt basin was a valley, inclosed by two longitudinal folds of the earth's crust, commencing at one end with the ocean by a shallow bar, over which, in autumn, the gales and high tides carried large quantities of sea-water; not sufficient, however, to replace the water lost by evaporation. For a long period only gypsum was deposited here; afterwards common salt was formed as well, which converted the gypsum into anhydrite, but which for a long time was re-dissolved every autumn by the dilution of the liquor, caused by rain and floods. Thus the thick crust of gypsum and anhydrite was formed which lines the bottom of the basin. Later on, the liquor became more and more concentrated; the crusts of common salt now became permanent, and the yearly deposits increased in thickness. The sursaturation of the liquor at the bottom caused the transformation of the common salt into rock salt (as first proved by Mohr). Just as we observe it now in the 'salt gardens' on the Mediterranean, the last portions of the summer salt contained a little gypsum, but the greatest quantity of gypsum was precipitated when the strong brine came into contact with fresh sea-water breaking over the bar, thus forming a distinct line of separation against the next year's deposits in the shape of the 'anhydrite strings.' Since there was less and less room in the basin for fresh sea-water, those strings decreased in thickness during this period, which must have lasted several thousands of years, during the later part of which the yearly deposits had an average thickness of 3½ inches. Owing to further concentration of the liquor the crusts of salt in the later part of summer were more and more mixed with Epsom salt, which appears also with the gypsum precipitated soon after by the influx of fresh sea-water. In this period, which must have lasted 500 or 600 years, *polyhalite*,  $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ , was formed. In the following way: some carnallite,  $KCl \cdot MgCl_2 \cdot 6H_2O$ , formed in summer, was at that period always decomposed in autumn by

fresh sea-water, and the potassium chloride thus set free and coming into contact with the deposited Epsom salt was converted into potassium sulphate, which met with enough magnesium and calcium sulphates to form polyhalite. Exceptionally, indeed, carnallite is actually found in that region. During the next period of 500 years, with  $\dots$  saturation, some carnallite was  $\dots$  but the principal deposit at that time consisted of *kieserite*  $MgSO_4 \cdot H_2O$ . It has been proved by Precht (Ber. 14, 2131) that from a concentrated solution of magnesium chloride, such as must have filled the basin at that period, the magnesium sulphate is separated by evaporation, not in the state of Epsom salts ( $MgSO_4 \cdot 7H_2O$ ), but in that of *kieserite*. This compound being insoluble, as well as the anhydrite, the formation of polyhalite was not any more possible.

During the fourth and last period of 500 years, when there was less room for the influx of fresh sea-water, the formation of *carnallite* got the upper hand. Pfeiffer has proved that that salt, and even hydrated magnesium chloride, can be made to crystallise by spontaneous evaporation at the temperature of hot summer days in our present climate. The formation of carnallite must have been still abundant, and a deep layer of mother liquor, in which magnesium chloride prevailed, must have been standing over the potash-bearing strata when new geological changes caused the eruption of a mighty mass of clayey mud, charged with organic substances, which sank to the ground, forming a layer of salt clay, 26 feet thick, which protected the underlying strata against a subsequent solution of the salts previously deposited, even after the mother-liquor had run off. The loss of that liquor accounts for the difference between the average composition of the Stassfurt deposits and that of the sea-water (comp. above). Wherever such accidental protection was not afforded, the surface-water must have re-dissolved the upper strata, which accounts for the general absence of mother-liquor salts in other localities.

Apart from Stassfurt, the following occurrences of potassium salts require mentioning:—

In 1866 at Kalusz, in Eastern Galicia, potassium salts were found in large quantities, principally consisting of sylvine and kainite, and a large manufacturing industry was commenced. But the quality of the salt proved inferior to the first samples, and in 1875 the works were discontinued, for various reasons, as being unable to compete with Stassfurt.

Small quantities of potassium salts, always of poor quality, have been found in the Punjab, in Persia, and in Colorado. None of these deposits gives any promise of industrial application.

The *rock-salt* in the mines round Stassfurt is not now obtained from the lower strata, where the admixture of anhydrite brings it down to 95 p.c., but from the upper (secondary) strata at Neu-Stassfurt, where it comes up to 99 p.c. of real sodium chloride. There is also a large quantity of pan-salt made in the neighbouring Schönebeck salt works.

The average composition of *crude carnallite* is :

	Per cent.
Potassium chloride . . . . .	15.7
Sodium chloride . . . . .	21.5
Magnesium chloride (with a little bromide) . . . . .	21.3
Calcium chloride . . . . .	0.3
Magnesium sulphate . . . . .	13.0
Insoluble (anhydrite, clay, &c.) . . . . .	2.0
Water . . . . .	26.2

Small quantities of rubidium (0.001-0.003 molecules), cesium and ammonium, and of bromine (0.005-0.01 mol.) are always present in carnallite.

It is sold on a basis of 16 p.c. potassium chloride; salts with less than 12 p.c. potassium chloride are hardly ever worked.

*Crude kainite* generally contains :

	Per cent.
Potassium sulphate . . . . .	24.0
Magnesium sulphate . . . . .	15.5
Magnesium chloride . . . . .	13.0
Sodium chloride . . . . .	31.0
Gypsum and clay . . . . .	1.5
Water . . . . .	14.0

*Kainite* is not very much worked now.

*Hartsalz* is a mixture of about 20 p.c. sylvine, 25 p.c. kieserite, and 55 p.c. rocksalt.

*Sylvinite* is the name given to crude kainite or hartsalz, if the percentage of potassium exceeds 13 p.c.  $K_2O$ .

*Crude sylvine* (not to be confounded with sylvinite) is a raw material of great importance, consisting of varying quantities of sylvine and rock-salt: the percentage of KCl varies from 25 to 50, or 90 p.c.

*Crude kieserite* is very impure, much more so than the residual product obtained in the manufacture of potassium chloride. Still, about 12,000 tons per annum are used.

*Boracite*, with 52 or 53 p.c. crystallised boracic acid, is obtained as a by-product.

#### *The manufacture of Potassium Chloride at Stassfurt.*

At first the importance of the strata found underlying the rock-salt at Stassfurt was not recognised, and it is principally due to the untiring exertions of Dr. A. Franck since 1860 that this was ultimately done. In 1861 he erected a small factory, and was immediately followed by Messrs. Vorster & Grüneberg, and soon after by Messrs. Leisler & Townsend. The last-mentioned factory—called the ‘English factory’—which was designed on the principle of introducing as much mechanical labour as possible in the process, was very important for the later development of that industry. In 1864 there were already 18, in 1872, 33 different potash works at Stassfurt, in 1887 the number was 35.

The raw material for the manufacture is the crude carnallite as supplied by the mines in tolerably uniform quality; its average composition has been stated above. The principles of working it up are as follows: carnallite,  $KCl \cdot MgCl_2 \cdot 6H_2O$ , is unstable in the presence of water: it is decomposed into a magma of very finely . . . . . and a solu-

tion of magnesium chloride, retaining but little KCl at a low temperature. On heating, the solution dissolves much more KCl, and on cooling the latter salt is separated in much larger crystals so long as the proportion of  $MgCl_2$  does not exceed three times that of KCl. When that proportion has been reached the liquor on further concentration yields a crop of carnallite, which at a low temperature is very little soluble in the remaining solution of magnesium chloride. Of the foreign salts present in crude carnallite, rock-salt is much less soluble in hot  $MgCl_2$  solution than KCl, and thus remains behind to a great extent; kieserite, which is insoluble as such but turns into soluble Epsom salts on heating with pure water, is prevented from so doing by the presence of magnesium chloride. The remaining substances are not of much consequence; some of them are quite insoluble.

Practically it has been found useful to treat the ground raw material, not with water, but with waste liquor from a previous operation in such quantity that it suffices for dissolving the carnallite present at a boiling heat; the solution is removed from the residue (the washings of a fresh solution) and is allowed to cool down, when it deposits about 80 p.c. of the potassium chloride; the mother-liquor, on further evaporation and cooling, yields the whole of the remaining KCl as a crop of carnallite which is decomposed by water as above. The products are purified in the manner described below.

The first operation, *dissolving the crude carnallite*, is the most important of all for the success of the manufacture. The result differs very much according to the quality of the crude carnallite, according to its state of division, according whether pure water or liquors obtained in other stages of the manufacture are employed, and also according to the duration of the operation. It is, in principle, preferable to effect the solution of carnallite as quickly as possible in order to dissolve less of the other salts. The quickest operation is undoubtedly that practised at the ‘English’ factory—crushing the crude carnallite into powder, and dissolving it in a close vessel at several atmospheres pressure with mechanical agitation. But this process causes too much rock-salt and even kieserite to be dissolved at the same time, and it also causes the formation of very much mud; hence most manufacturers work at the ordinary atmospheric pressure, or very little above it, without mechanical agitation, and employ coarsely-crushed carnallite.

Fig. 3 shows one of the usual descriptions of dissolver. The true bottom *g* is slanting, the false bottom *e* is horizontal. The latter is perforated by a large number of holes  $\frac{1}{4}$ -inch wide; in the centre there is a double-hinged trap-door *b*, also perforated. The two halves of this door are suspended from the hinged arm *a*; they are closed when *a* is in the upright position, in which it is kept by the vertical rod *h*. When the solution has been run off through *c*, the rod *h* is knocked away, arm *a* to turn over, and the two halves of *b* fall down. The residue is now easily washed down from *e*, and cleared out through *f* by a strong jet of water passed all over *e* by a steam-pipe *d*, with two rows of holes, is carried

round the central opening of *e*. The conical shape of the bottom has the two-fold advantage that the liquor can be run off completely and that the residue can be got

Formerly the dissolvers were of iron, but since it has been found that iron resists much better than

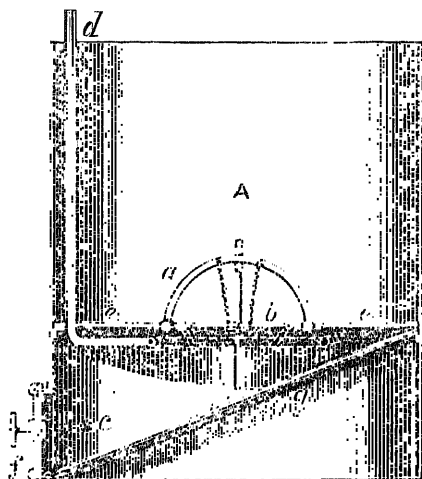


FIG. 3.

the salts, it has become usual to employ cast-iron cylinders, with a conical bottom, provided with a sieve, below which the steam is introduced, the head of the steam-pipe being closed by a bulb with many perforations.

Where it is considered desirable to dissolve under a slight pressure, the top of the dissolver is covered in, the man-hole being closed during the work, or else a tube reaches down from the cover into the liquid, nearly to the false bottom, in order to introduce the salt, and to produce some degree of steam pressure in the apparatus. The waste steam can be employed for heating up the liquor in another pan. Such vessels, of about 350 cubic feet, admit of working up 50 tons of salt and more in 24 hours.

The liquor employed for dissolving (called 'Löselaug') is a mixture of various liquors resulting in the manufacture, especially the washings of the first residue, and those of the second, as well as various mother-liquors, of a sp.gr. 1.268 to 1.279; through being heated up by waste steam, the liquor comes down to 1.257, and is used in this state. This liquor is run into the dissolver until this is half full; steam is injected until the liquor is brought to boil, and only then the crude carnallite is introduced. For each 100 cubic feet of tank room, from 30 to 36, or at most 42 cwt. of carnallite can be charged. The solution is first brought to sp.gr. 1.313 to 1.337 (measured hot and in the muddy state), but in this state the residue would be very difficult to treat; there would be considerable loss of potassium chloride by crystallising out before the liquor was clarified, and the potassium chloride obtained in the coolers would be contaminated by newly-formed carnallite. To avoid

this, the solution is diluted to sp.gr. 1.28 or 1.30 (measured hot and muddy). The operation of dissolving ought not to last more than half an hour, or, including other necessary work, 2 hours, so that 12 operations can be made in 24 hours.

The solution must now be clarified by allowing it to rest for an hour or two in settling-vessels, and drawing off the clear portion by means of a drop-siphon. The clarifying operation can be promoted by sprinkling a little milk of lime on the surface, which precipitates some magnesia, the latter carrying down the other impurities. The residue must be once or twice boiled up with fresh water, if the crude carnallite had been employed in lumps of the size of a fist; if, as now usual, it had been more finely crushed, it is either removed at once, or it is previously boiled up with a small quantity of mother-liquor, the resulting liquor being utilised as part of the dissolving liquor for fresh carnallite, or by cooling down, when it yields weak potassium chloride.

The following analyses show the composition of the ultimate residue, forming from 26 to 30 parts of the crude carnallite:

	<i>a</i>	<i>b</i>	<i>c</i>
Potassium chloride .	5.25	3.0	2.2
Sodium chloride .	47.00	45.0	54.8
Magnesium chloride .	3.85	2.0	2.5
Magnesium sulphate .	29.25	38.0	22.9
Calcium sulphate .	2.15	0.7	1.8
Insoluble .	6.00	5.3	5.0
Combined water .	6.50	6.0	10.8

100.00 100.0 100.0

*a* is a product as formerly obtained, *b* and *c* more recent products of different works. The 'insoluble' is mostly anhydrous calcium sulphate, clay, boracite, and sand.

The residue was formerly allowed to accumulate in large heaps, part of which only was utilised for manufacturing kieserite and sodium sulphates; where there was not room enough for the residue, it had to be washed away by a stream of water. It is now employed for filling up the old carnallite mines, since this has been required by Government regulations in order to prevent subsidences of the soil.

A different kind of residue is obtained by thoroughly settling the liquid in tanks, protected against cooling, and drawing off the clear liquor by means of a drop-siphon. This second residue, the 'muddy', consists essentially of potassium chloride, a little anhydrite, clay, calcium sulphate, &c.; also by potassium chloride. It is separated from the liquor by means of a vacuum filter, or, preferably, of a filter-press in which it can also be washed by water, which removes the potassium chloride, affecting the other salts to a great extent. Even then from 4 to 26 p.c. of potassium, calculated as chloride, are retained in the mud, probably in the shape of potassium magnesium sulphate.

Formerly the clear liquor was purposely allowed to cool down to some extent, say to a temperature of 80° or even less, before being run into the crystallising vessels, in order to precipitate some sodium chloride. But since the

solution is now made by means of mother-liquors, the clear liquor contains less NaCl, and is generally at once employed for crystallisation. The following analyses refer, I. to a liquor made with water, of sp.gr. 1.3 (at 105°) in the muddy, and 1.284 in the clarified, state; II. to a liquor made with mother-liquor, of sp.gr. 1.313 (at 105°) before being diluted with water; III. shows the maximum and minimum percentages found in ordinary liquors:

	I.	II.	III.
Potassium chloride . . .	11.08	10.70	8-14
Sodium chloride . . .	5.68	4.20	4-8
Magnesium chloride . . .	17.65	24.60	15-25
Magnesium sulphate . . .	2.92	1.50	1.5-5
Water . . .	62.67	59.00	—
1 cubic metre contained . . .	142.2	140.5 kilo.	potassium chloride.

The vessels (coolers) are wrought-iron, sizes, usually from 150 to 300 cubic feet capacity—e.g.  $7 \times 8 \times 4$  feet, with bottoms slanting a little to one side, where there is a plug for running off the mother-liquor. They are best placed a little above the floor, so that the air can circulate underneath, and in summer this should be promoted by Venetian shutters in the building. If the cooling takes place too quickly, the crystals are too small and muddy. Two or three days ought to suffice.

The salt first precipitating carries down such suspended matters as had not been removed by settling; hence such 'bottom salts' are less pure than the 'side salts' crystallising afterwards. The quantity of the latter is sometimes increased by suspending bundles of wire in the coolers, but this is now done but rarely, as the extra labour is hardly recompensed by the advantages of that process. When the cooling has been finished, the mother-liquor is siphoned off, or is run off by a plug, exactly as in the manufacture of soda crystals.

The proportion of bottom salts to side salts ranges from 2 down to 1 part of the former to 1 of the latter; some analyses of this 'first product' run as follows:—

	Bottom salts		Side salts		Mixtures of both
	Drained	Dry	Drained	Dry	
Potassium chloride	50.2	59.76	60.8	58.31	64-69
Sodium chloride	27.0	32.14	24.4	27.42	28-22
Magnesium chloride	4.3	5.12	2.8	3.15	7.5-8.5
sulphate	2.0	2.33	1.0	1.12	0.5-0.5
Insoluble	0.5	0.60	—	—	—
Water	16.0	—	11.0	—	—

The mother-liquor drained off from the crystals of KCl retains about  $\frac{1}{4}$  of the total KCl, most of which is recoverable by evaporation and cooling the concentrated liquor.

The following are analyses of the 'first mother-liquor,' as remaining behind from the 'first product' (I. former process, II. present process):

	I.	II.
Specific gravity at 20°	1.273	1.279
Potassium chloride . . .	5.50	4.50 p.c.
Sodium chloride . . .	3.80	3.20 "
Magnesium chloride . . .	19.90	22.80 "
Magnesium sulphate . . .	2.70	2.15 "
Water . . .	68.10	67.35 "

Part of it is employed for dissolving fresh crude salts as mentioned above; the remainder is concentrated by evaporation until nearly all the KCl can be obtained on cooling as artificial carnallite. This concentration was formerly carried out in two stages—first to sp.gr. 1.279 (when low-grade potassium chloride was obtained), and then to 1.325; but now, since coal is dearer and lower prices are obtained for the product, it is found best to concentrate at once to 1.325, which means evaporating about one-third of the bulk of the liquor, till the boiling-point reaches 123°.

The evaporation must be carried on in such manner that the heating surfaces are not covered by crusts of salts, and, of course, in such a way that the fuel is utilised in the best possible manner. Evaporating by means of steam-coils has been found less economical than by means of open fires. Passing over the antiquated modes of concentration as formerly employed at Stassfurt, we shall describe the more recent process. It is now usual to carry on the evaporation successively in two different kinds of apparatus—namely, first, up to the point where salts would be separated in the boiling liquor in ordinary two-fueled steam boilers, the steam being utilised for dissolving. In lieu of this the first

with very great advantage, carried on in combination with such as have been in use at Stassfurt works, and here and there the second stage of concentration is separated during the process, is best carried on in open pans, heated by internal flues, as shown on a scale of  $\frac{1}{2}$  in Figs. 4 and 5, which at the same time illustrate the 'step-grates,' universally employed at Stassfurt for the friable brown coal found in the neighbourhood. The flame, generated on the grate *g*, passes through the central wrought-iron tube *a* and back again through the lateral tubes *bb* into the brick flues *ll*. The very strong boiling of the liquor prevents the formation of any crusts of salts on the tubes *a* and *b*.

It has now become general to cover in these pans, and to utilize the steam escaping from them in various ways. The consumption of fuel (lignite) has been greatly diminished by the introduction

The first stage of concentration, that in which no salts are separated, is carried on above sp.gr. 1.26; during this stage the evaporation is continuous, fresh liquor being run into the boiler to keep it up to the same level. In the second stage the salts were formerly removed by fishing, which might be done more advantageously by mechanical means. It is, however, usual to boil down to sp.gr. 1.32 or 1.33 in winter, 1.33 or 1.345 in summer (testing the liquor in the muddy and hot state), to allow it an hour's settling, and to run it then into a cooler. The fished salts and the settling mud are washed with water, the washings being utilised for dissolving crude salts; but even then they contain from 7 to 12 p.c. potassium, calculated as chloride, together with 50 to 66 p.c. of sodium chloride, and cause an appreciable loss, as it is not easy to extract that potassium chloride with advantage. The mother-liquor contains about 5.5 to 6 KCl, 2-3% NaCl, and 6-3 MgSO<sub>4</sub>, and 59-64 H<sub>2</sub>O. It is run into coolers, and left there during

three or four days. At first—that is, down to a temperature of 65°—principally sodium chloride crystallises out, and this can be kept out by a previous cooling down to that temperature. On further cooling, ‘artificial carnallite’ is separated, usually containing from 18 to 22 p.c. KCl, equal to 67–82 p.c. of real carnallite, together with a little NaCl, MgCl<sub>2</sub>, and MgSO<sub>4</sub>. This salt is dissolved in water, brought to boiling heat by means of open steam, till the sp.gr.=1.268 (at 105°) has been attained, and a little milk of lime is added at the finish, in order to remove any iron present and to mechanically clear the liquid.

The dissolving and settling last an hour each, three or four days. Some ‘artificial carnallite’ is decomposed in the cold way, by ‘settling’ it with cold water until most of the NaCl is dissolved, and separating this solution by suction from the solid KCl remaining behind. The result of the operation is solid potassium chloride, ‘second product,’ and a ‘second mother-liquor,’ of sp.gr. 1.257 (measured cold), with 3–4 p.c. KCl, which is usually added to the first mother-liquor in the concentrating pans.

The quantity of second product amounts

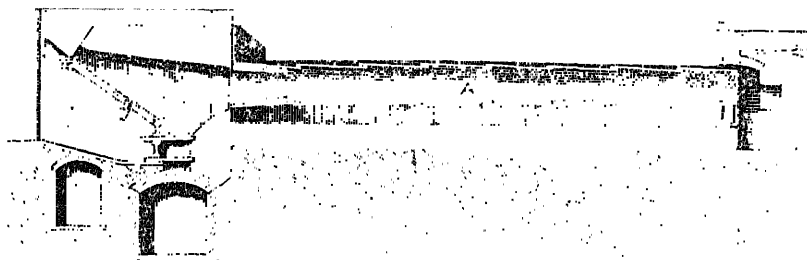


FIG. 4.

to about 20 p.c. of the total make of potassium chloride; its analyses show its comparative purity:

*Bottom salts.*

	Drained	Dry
Potassium chloride . . .	67.0	77.38
Sodium chloride . . .	13.7	15.82
Magnesium chloride . . .	5.3	6.11
Magnesium sulphate . . .	0.6	0.09
Water . . .	13.4	—

*Side salts.*

	Drained	Dry
Potassium chloride . . .	80.2	89.02
Sodium chloride . . .	7.0	7.77
Magnesium chloride . . .	2.6	2.88
Magnesium sulphate . . .	0.3	0.33
Water . . .	9.9	—

The following are tests of the ‘final mother-liquor’—*i.e.* that which remains after the crystallisation of the artificial carnallite:

	Former process	Present process
Specific gravity . . .	1.310	1.313
Potassium chloride . . .	1.25	1.20
Sodium chloride . . .	0.95	1.20
Magnesium chloride . . .	29.50	28.05
Magnesium bromide . . .	0.30	0.31
Magnesium sulphate . . .	2.22	3.10
Water . . .	55.78	60.14

Its quantity is 5 or 7 cubic metres to each 10 tons of crude carnallite, and it is now usually worked for *bromine* (*q.v.*); partly also for *magnesium chloride* (*v. infra*).

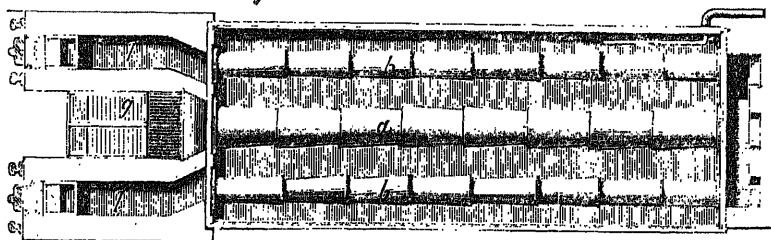


FIG. 5.

*Purification of potassium chloride.* This is always performed by washing, utilising the fact that at low temperatures the solubility of KCl decreases very much more than that of NaCl, MgCl<sub>2</sub>, &c., and that the contact of water with those salts itself causes a lowering of the temperature (sometimes amounting to 10°), so that the water in winter would be turned into ice if it were not employed in the tepid state.

The washing of the salt takes place in iron vessels, provided with a false bottom, upon which the salt rests. This false bottom is made of wood or of iron plates, perforated with  $\frac{3}{8}$ -in. holes, and is covered with a web of split cane. employed for washing is salt by means of an elastic tube, ending in a rose, and the liquor is removed from underneath



the false bottom by means of a tap or plug. In Fig. 6, *a* is the tub, *a* a man-hole through which the washed salt is removed at the end, *b* the false bottom, *c* the tube and rose for washing, *d* the charging bogie, *e* the running-off tap.

The tub is completely filled with salt, and this is first washed with washing-liquor from a former operation, which in this way yields some of the KCl previously taken up, and takes up NaCl in this stead. After having twice served in this way, the liquor is used for dissolving crude carnallite, in the first operation described above. The first liquor is run off at once, until the liquor is displaced; the tap *e* is now run on to the top of the salt, leaving it in contact with the same for two hours, and then running it off. This is repeated with once-used liquor, and last of all with fresh water. The washing-tubs are best suspended from the staging by means of trunnions, with toothed-wheels for turning them on

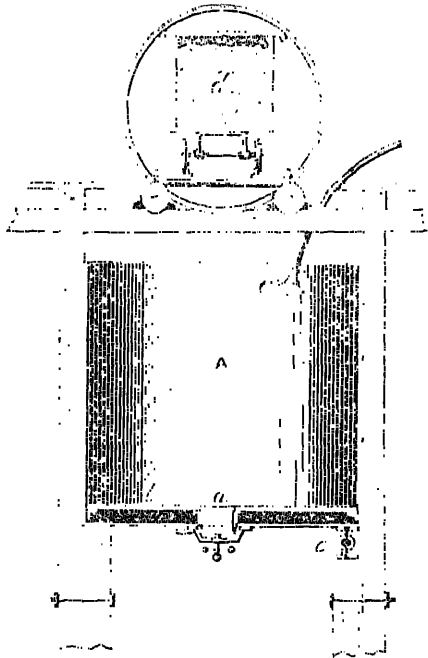


Fig. 6.

their axis at the end of the operation, for the purpose of emptying out the washed potassium chloride.

The washing operation is not advantageous with products containing less than 50 p.c. KCl; such products are better purified by re-crystallisation.

The washed salt naturally contains a considerable quantity of water. By simple draining this can be got rid of down to 7 or 9 p.c., by centrifuging to 5 p.c. The remainder is removed by heating, which was formerly mostly done in reverberatory furnaces. The modern method of use now is shown in Fig. 7.

Upon the foundation *i* a cast-iron drum *h* is mounted, the hollow part of which is heated by steam through *m*, whilst at *n* there is a steam-trap for the removal of the condensed

water. In the centre there is a perpendicular shaft, *l* revolving in a bearing protected by a cap. This shaft is moved by means of the pulleys *u* and the bevel wheels *k*, and it carries

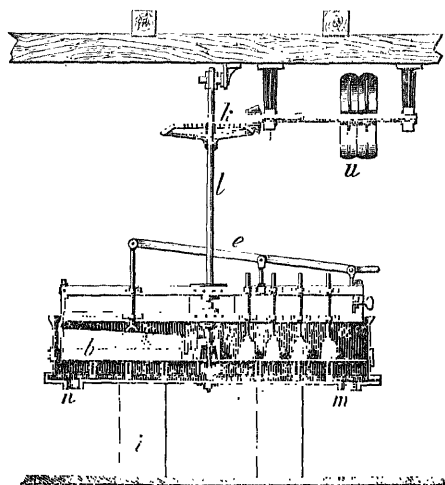


Fig. 7.

the horizontal arm *t*, to which are attached a number of plough-shares *a*, a crushing-roll *b*, and a discharging-scraper *c*, set in motion by handle *e* and lever *s*. The last-mentioned part serves at the end of the drying operation for moving the salt towards the circumference, where it falls through an opening, kept shut up to this time by a slide, into a shoot and bag attached to it. Each charge yields 60 kilos. dry salt, and each drying-plate turns out from 2 to 2½ tons per day of 27 hours. With wrought-iron plates of 8 feet diameter, which transmit the heat more easily, nearly 5 tons can be dried in 24 hours. In some places Thelen's mechanical drying-pans are employed, which are heated by direct fire, and yield about 15 tons per 27 hours, with an expenditure of 8 to 10 p.c. of brown coal (the fuel value of which is not quite one-half that of ordinary coal).

Whichever apparatus may be employed, the formation of crusts cannot be entirely avoided. These are removed once a day, and are crushed in order to be sold as manure salts, containing about 70 p.c. KCl.

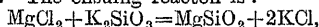
The drying is usually carried up to 2 p.c. water for low grades, or 0.5 p.c. for high grades; but it is best to leave the salt a short time in a cool, dry place before packing. It is then crushed between rolls, sifted, and packed into jute bags, holding 100 kilos. each.

#### ANALYSES OF COMMERCIAL POTASSIUM CHLORIDE.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
KCl .	80.85	89.78	82.00	96.5	84.30	98.58
NaCl .	16.25	8.10	16.00	2.0	12.98	0.22
MgCl <sub>2</sub>	0.20	0.10	0.40	0.2	0.19	0.07
MgSO <sub>4</sub>	0.59	0.33	0.30	0.2	0.10	0.12
CaSO <sub>4</sub>	0.18	0.27	0.25	0.3	0.22	0.24
Insol.	0.33	0.32	0.15	0.2	0.23	0.31
Water	1.60	1.10	0.90	0.6	1.98	0.46

*a* and *b* manufactured in 1869, *c* and *d* in 1873, *e* and *f* in 1884.

Another process for treating carnallite has been patented by Schliephacke and Riemann (D. R. P. 43932). They smelt raw carnallite in a cupola furnace with felspar or granite, and run the liquid product into cold water, whereby it is granulated and the soluble salts are more easily extracted. Magnesium silicate remains behind in an insoluble state; the solution, which contains the potassium as silicate, is treated with a solution of crude carnallite or waste liquors from the manufacture of potassium chloride. The ensuing reaction is:



so that only potassium chloride remains in solution. The gases escaping from the throat of the cupola furnace are to be treated for chlorine and hydrochloric acid. (This ingenious process does not seem to have been practically carried out.)

**Manufacture of potassium chloride from sylvine.**—This is an exceedingly simple matter, since a hot saturated solution of  $\text{KCl} + \text{NaCl}$  on cooling allows nothing but  $\text{KCl}$  to crystallise out. Ground sylvine is dissolved in the same way as described in the case of carnallite; the solution, if necessary, is cleared by subsidence and allowed to crystallise, just as the solutions obtained from carnallite. The resulting potassium chloride tests 92–94 p.c.  $\text{KCl}$ , even without washing, and by washing can be brought up to 98 p.c. Experience has shown that the crude sylvine should not contain more than  $\frac{1}{4}$  p.c.  $\text{MgO}$  (in the shape of kieserite); if it contains more, both  $\text{MgO}$  and  $\text{SO}_3$  are removed by adding milk of lime. A modified process for obtaining sylvine from mixtures with rocksalt, &c., is described in the D. R. P. 132474 of Speyerer.

The manufacture of  $\text{KCl}$  from *haltsalz* is carried on in a similar manner, e.g. by Tünger's D. R. P. 102075; but as this material is of very varying composition, the special rules for working must be fixed from case to case.

Meyerhoffer (D. R. P. 91906) obtains potassium chloride from carnallite by heating this to about  $167^\circ$ . About three-quarters of the  $\text{KCl}$  is thus obtained in a solid form, whilst the remainder and all the  $\text{MgCl}_2$  remains in solution which, on cooling down to about  $115^\circ$ , deposits nearly all the  $\text{KCl}$  and leaves only  $\text{MgCl}_2$  in solution. The same inventor (D. R. P. 92812) purifies carnallite by heating to about  $265^\circ$  and removing the fused carnallite by presses from the residue. Further improvements are described in his D. R. PP. 98344, 99957, 109101.

The Salzbergwerk Neustassfurt (D. R. P. 138562) dissolves the carnallite *in situ* underground by means of tepid water, the solution being pumped up.

Maurer (D. R. P. 166558) gives detailed prescriptions for the preparation of potassium chloride from the crude Stassfurt salts.

Haag and Glienicke (D. R. P. 163413) fuse the carnallite out of the crude salts by electric heating.

#### BY-PRODUCTS OF THE STASSFURT POTASH INDUSTRY.

1. **Kieserite.** This insoluble body,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , which becomes soluble only by prolonged con-

tact with water, when it passes over by an intermediate stage into Epsom salts  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , is naturally left behind in the residues from dissolving crude carnallite and settling the liquor. Most of it is lost in the shape of pit heaps, &c.; only then is it regularly recovered by the potash manufactures, when they are obliged to get rid of their residues by washing away, because in this case the law compels them to retain the insoluble portions; otherwise kieserite is only prepared when there is special demand for it. Since it soon passes over into the above-mentioned intermediate stage, it must be made from fresh residues, which is done by subjecting them to a combined levigating and sifting process. A convenient apparatus for this purpose is shown on a scale of  $\frac{1}{50}$  in Fig. 8, where *g* is a hopper containing the residues, which rest on a grating; the water issuing from *b* produces a muddy liquor, which meets the slanting sieve *c*; the coarser portions run off at *f*, the finer ones

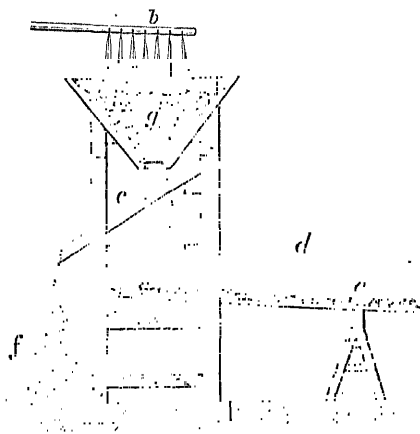


FIG. 8.

pass through into the slanting shoot *d*, where at first anhydrite settles; further on, at *e*, kieserite is deposited together with a little boracite, remains suspended till the last, and is kept back in special settling basins. Of course, in lieu of the slanting shoot *d*, several settling troughs with overflows can be employed.

The kieserite must be removed at short intervals and put into iron or wooden moulds, where it solidifies after fifteen minutes, so far that the blocks can be taken out. The solidification (which is a process similar to that occurring with gypsum, a chemical combination with water taking place) proceeds with evolution of heat; in a few days the blocks, weighing  $\frac{1}{4}$  to  $\frac{1}{2}$  cwt., are as hard as stone, and can be sent out in this state without being packed in casks, bags, or the like. After a lapse of time, however, they fall to powder by the attraction of atmospheric moisture and formation of Epsom salts.

The quality of block kieserite naturally varies, according to the more or less careful separation from other matters; a minimum of 55 p.c. magnesium sulphate is, frequently guaranteed. When it is required in the ground state, it is first calcined in a reverberatory furnace.

## ANALYSES OF KIESERITE BLOCKS.

	Fresh		Calcined	
	a	b	a	b
Magnesium sulphate	60.20	58.0	81.5	77.8
Sodium chloride	1.55	2.1	2.1	2.7
Insoluble (anhydrite, &c.)	10.63	13.5	14.4	17.0
Water	27.62	26.4	2.0	2.5

The yield of block kieserite is about 10 p.c. of the crude carnallite. With careful work it can be got up to 12 p.c., but this is scarcely ever done, because at present only one-tenth of the residues is worked for it, the demand not being equal to the supply.

A small quantity of block kieserite is converted into *calcined kieserite*, with a guaranteed minimum percentage of 70 p.c.  $\text{MgSO}_4$ , by calcining in ordinary reverberatory furnaces, grinding and packing in bags.

The Gewerbschaft Carlsfund (D. R. P. 166187) obtains kieserite from its mixture with common salt by digestion with more or less concentrated salt solutions.

*Applications of kieserite.* Most of it is employed for making Epsom salts, some of it for potassium sulphate. We mention the following attempts at utilising the substance in other ways.

G. Clemm (in 1863) calcined the kieserite, preferably mixed with coal, in the presence of steam, and carried the vapours into vitrol-chambers; magnesia remains behind (in a very impure state). By a similar process Precht (in 1881) makes basic linings for the steel process. Several other inventors have tried to utilise either the sulphuric acid or the magnesia, but hitherto not to any appreciable extent.

The only extensive employment of kieserite is that of converting it into *Epsom salts*, of which about 25,000 tons per annum are made in Germany, and a considerable quantity in England and in the United States. The process consists simply in causing the kieserite to take up more water, preparing a solution, and allowing this to crystallise. Formerly the process was promoted by calcining the kieserite, after which it is at once soluble in water; but this object can be equally attained by the prolonged application of steam, or, even more cheaply, by soaking the crushed kieserite with the mother-liquor from the Epsom salts, when it gradually passes over into the heptahydrated salt, with great increase of bulk. A solution is now prepared by water and steam, of sp.gr. 1.31 to 1.325 (tested hot and muddy). This is clarified in settlers, where it is kept about an hour; the last particles of gypsum and clay, floating in the liquor, are removed by wood-lined filter-presses; (if necessary concentrated in means of lead coils) is run into lead-lined iron or wooden crystallising vessels.

After three or four days the crystallisation is finished; the crystals are all the finer the more concentrated the liquor had been, and they are

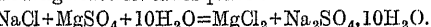
at first practically free from sodium chloride. The mother-liquor inferior to this is run to waste; the last liquor is run to waste.

The crystals of Epsom salts are in England merely drained by a centrifugal machine, turning out 2 tons per day, and the product, still containing 3 or 5 p.c. of moisture, is directly packed into casks; in Germany they are dried in a room heated by exhaust steam, &c., at a temperature not exceeding  $45^\circ$ , the dry salt is passed through wooden rollers, leaving a space of  $\frac{3}{8}$  inch, so that only the lumps are crushed; it then passes through a sieve, and from this into the casks.

The favourite shape of Epsom salts is that of fine needles, of silk-like lustre, which are most easily formed by moderately quick cooling of a concentrated solution. The coarser crystals are separated by sifting and re-dissolved, or sold as second quality.

The principal application of Epsom salts was formerly the medicinal one, which, of course, did not amount to large quantities. At present the greater portion of it is employed in finishing textile fabrics, especially calico. Other applications (mostly only proposed or temporarily tried) are those for replacing the 'pearl-hardening' in soap-making (mixed with lime), for preparing sulphate, for purifying beet-root sugar juice, for rendering fabrics fire-proof, for manufacturing sulphur trioxide, in several soda-making processes, and so forth.

2. **Glauber's salt**  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , can be made by Balard's process—that is, by mixing a solution of sodium chloride with sulphate to a temperature of  $100^\circ\text{F}$ , the following reaction takes place:



The Glauber's salt crystallises out, magnesium chloride remaining in solution. At the mouth of the Rhone this is done by artificial cold; at Stassfurt it can be done without that during the winter months. The material is present in the residues from dissolving crude carnallite, the composition of which has been stated on page 342. Just the weathered residue which is no more adapted for the treatment for kieserite, is most suitable for the above process, and from 50,000 to 75,000 tons of Glauber's salt might thus be made per annum; but the quantity actually produced is only about 10,000 tons, and varies very much according to the nature of the season.

The residue is dissolved in various ways; the longer it has been exposed to the weather, the more easily the solution takes place. Usually the residue heaps are lixiviated on the spot by means of hot water, the solution being caught in a trench made at the bottom of the heap. If the proportion is not  $= 2\text{NaCl}$  to  $1\text{MgSO}_4$ , the composition of the liquor is corrected and its strength is brought up to about 1.269 at  $33^\circ$ . The solution is clarified by settling, and is exposed to the cold of a winter's night, always under the open sky. Ordinary coolers are not so well adapted to this purpose as large, shallow tanks, made of pine-wood planks, the joints being made tight by caulking with hemp and tar. These tanks are erected on wooden pillars, and are sometimes 100 by 100 feet square, and 8 inches deep. During summer, when they are not used, they are kept filled with a solution of

common salt. In such shallow tanks the liquor is better cooled down during the night, 1 cubic metre often yielding 150 to 180 kilos. of crystals. The mother-liquor is run off in the early morning, before it can get warm again; it shows the sp.gr. 1.205 to 1.225.

3. **Magnesium chloride**  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , is obtained by evaporating the 'final mother-liquor' in the same description of apparatus as described above for the treatment of carnallite liquors, usually in pans with flame-pipes, to a b.p. of  $157^\circ$  which corresponds to sp.gr. 1.388 or 1.40 (taken hot), allowing to settle for an hour, and running into a cooler, whereupon the whole mass solidifies in a few days. It is broken into large pieces, which are put into casks; the empty space is filled up by a hot, strong solution of magnesium chloride, which on cooling, cements the whole into a solid mass. Sometimes the dry salt is melted for some time in a furnace, to expel some more water, but if this is driven too far, hydrochloric acid escapes as well. This process is much dearer than the first, and there is not much gained by it. A colourless, glassy product is obtained by boiling down only to sp.gr. 1.44, oxidising the ferrous salts by adding potassium chlorate (of which about 3 kilos. is required for a charge of 40 cubic metres of concentrated solution), heating further until a b.p. of  $157^\circ$  has been reached, and precipitating the iron by the addition of an excess of milk of lime (of which about 130 kilos.  $\text{CaO}$  will be required for 40 cubic metres of liquor), and cooling down to about  $125^\circ$ . The liquid is then run through the bung-hole into petroleum casks, in which it solidifies, and is sent out in this state. The analyses show:

	Boiled down to sp.gr. 1.388	Boiled down to sp.gr. 1.44
Magnesium chloride	45.74	51.05
Potassium chloride	1.35	1.38
Sodium chloride	0.25	0.27
Magnesium sulphate	0.15	0.10
Water	52.51	47.20

Since one ton of the product can be obtained from three (or, with care, from  $2\frac{1}{2}$ ) tons of crude carnallite, enormous quantities might be made at Stassfurt; but actually only about 12,000 to 16,000 tons are made, and are principally employed for dressing (lubricating) the rollers of the mangle. A very large number of uses have been proposed, in order to utilise either the chlorine, or the magnesia, or both. We mention here the following applications: as a disinfectant; for precipitating waste soap-lyes; for carbonising wool; for making patent fuel; for magnesia cement; for preparing magnesia, principally as 'basic lining' in the manufacture of steel; for manufacturing barium chloride.

**Crystallised magnesium chloride** is made by evaporating only to sp.gr. 1.42 and pouring the liquor into casks, already containing blocks of  $\text{MgCl}_2$  crystals, between which it solidifies. The crystal cakes contain about 43.0 p.c.  $\text{MgCl}_2$ , 1.3  $\text{KCl}$ , 1.2  $\text{NaCl}$ , 3.4  $\text{MgSO}_4$ , 51.1  $\text{H}_2\text{O}$ .

**Magnesia and hydrochloric acid** is made from magnesium chloride by two firms by means of secret processes. Probably the  $\text{MgCl}_2$  is first converted into oxychloride, and this is then heated by gases containing a large quantity of steam.

**Magnesia** alone is made from magnesium chloride liquor by means of lime, in two stages,

powder and removing the precipitate; second, adding more lime to decompose the  $\text{MgCl}_2$  into  $\text{MgO}$  and  $\text{CaCl}_2$ .

4. **Bromine** is largely made from the final mother-liquor of the Stassfurt works, which contains about 0.25 or 0.20 p.c. of it in the state of  $\text{MgBr}_2$ ; cf. the article **BROMINE**.

Part of the  $\text{MgBr}_2$  is converted into the iron compound  $\text{Fe}_3\text{Br}_2$  and sent out in this state to the bromine works, or into the bromides of potassium, sodium, and ammonium.

5. **Boric acid** is made from boracite or stassfurtite,  $2\text{Mg}_3\text{B}_6\text{O}_{15} \cdot \text{MgCl}_2$ , of which about 300 tons per annum is obtained at Stassfurt. It is dissolved in concentrated hot hydrochloric acid; the clarified solution is run into wooden coolers, lined with lead, where boric acid crystallises out. The crude acid is purified by washing or recrystallising. 100 parts of commercial boracite yield about 82 to 85 parts of crystallised boric acid  $\text{H}_3\text{BO}_3$ , which is partly sold as such, and partly converted into the sodium salt, known in trade as borax (*q.v.*).

6. **Potassic manures (artificial fertilisers)** are made from all the by-products of the Stassfurt manufacturers, as well as from minerals specially got for this purpose, especially kainite. The manufacturing operations consist merely in grinding, drying, calcining, and effecting a proper mixture to bring the product up to the guaranteed percentage of potash. Potassium sulphate is much better for this purpose than chloride, and magnesium chloride in the free state is absolutely injurious to vegetable life. Hence kainite and schoenite (*cf. Potassium sulphate*) are most usually employed as manures; but low-grade potassium chloride is also frequently sold for this purpose (*v. FERTILISERS*).

**Potassium chloride from the manufacture of sea-salt.**

... manufacture of ... in the 'salt ... It has, however, been worked out to great perfection in at least one locality, at Giraud-en-Camargue, at the mouth of the Rhone, originally by Balard, later on by Merle and Pechiney. Descriptions of this industry have been given by Wurtz (Hofmann's Bericht über die Wiener Ausstellung, 1875, [1] 410) and Lange (Chemische Industrie, 1883, 225). We quote here only those portions referring specially to potassium chloride.

From each cubic metre of sea-water, after obtaining the salt, 64 litres of mother-liquor, testing  $27^\circ\text{Bé}$ , remains behind. This mother-liquor is concentrated by solar heat to  $32\frac{1}{2}^\circ\text{Bé}$ ; the salt ... this operation is of inferior ... p.c.  $\text{NaCl}$ ), and is not utilized. But on further evaporating, by solar heat, from  $32.5^\circ$  to  $35^\circ\text{Bé}$ , a mixture of sodium chloride with nearly its equivalent of magnesium sulphate is separated, which is known as 'sels mixtes,' and is worked up in various ways, especially for Glauber's salts, by artificial cold (*p. 348*). The liquor of  $35^\circ\text{Bé}$  is kept during the winter in very large shallow tanks, where the temperature is prevented from falling below  $12^\circ\text{C}$ .; in this

case only Epsom salt crystallises out, but no carnallite. The new mother-liquor, testing 33°Bé., of which 16 litres per cubic metre of seawater has remained, is further evaporated by artificial heat in a Porion's furnace until it shows 37°Bé., tested hot. On the other hand, magnesium chloride solution, obtained at a later stage as a by-product, is evaporated in ordinary open pans to 40°Bé. Both hot liquors are run at the same time into an iron mixing-pan, taking care to maintain an excess of magnesium chloride. This causes at once a precipitate of 'sels mixtes' (cf. above), which are removed by a dredging apparatus. The hot liquor remaining behind still contains all the potassium salt; this is, however, separated on cooling in the form of artificial carnallite, owing to the presence of so much magnesium chloride, most of which is left in the cooled-down mother-liquor. This artificial carnallite, being in the state of fine mud, is easily decomposed by agitation with cold water, when magnesium chloride enters into solution and potassium chloride is left behind in the solid state. By systematic washing the latter can be brought up to 82 p.c. KCl.

Interesting and ingenious as this process is (in reality it is much more complicated than would appear from the preceding short description), it cannot very well compete with the Stassfurt industry, based as this is upon the natural accumulation of similar products through thousands of years. Hence Balard's process has not made its way elsewhere, and is not likely to do so.

*Potassium chloride from kelp.* In the manufacture of iodine from kelp—that is, the ashes of sea-weed—as obtained on the coasts of Scotland and Normandy, a large quantity of potassium salts is obtained, which, previously to the working of the Stassfurt deposits, was one of the principal sources of these salts for technical purposes. The liquor obtained by lixiviating the kelp is concentrated by evaporation in several stages, and thus yields several crops of crystals. The first crop, a mixture of potassium sulphate and common

alkaline sulphates and carbonates, which is fished out from the pans and sold as 'kelp salt'; on cooling, a crop of potassium chloride is obtained. The latter can be brought up to upwards of 90 p.c., and formerly about 2500 or 3000 tons of it was made per annum; but the development of the Stassfurt industry has mostly compelled the iodine manufacturers to give up the separation of the potassium salts in the pure state, and to utilise the rough mixture of those salts for agricultural purposes.

*Potassium chloride from beet-root vinasse.*  
This product, which always contains potassium sulphate and foreign salts, is described further on, under *Potash from beet-root vinasse*.

**Potassium bromide** KBr can be made in various ways, always starting from the bromine, obtained in America, in Scotland, or at Stassfurt. Only two of these processes have come into practical use.

The first consists in dissolving bromine in a solution of potassium hydroxide, which ought to be as pure as possible, evaporating the solution.

ultimately with addition of a little charcoal, and igniting the mixture. At first the reaction is as follows:  $6\text{KOH} + 6\text{Br} = 5\text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{O}$ . On igniting, the charcoal reduces the bromate to bromide. The mass is dissolved in water, filtered, and the potassium bromide obtained by evaporation and crystallisation.

This process suffers from the drawback that the mass decrepitates strongly on drying, and further losses through volatilisation, &c., cannot be avoided. Hence another process is almost exclusively employed now, similar to that used for potassium iodide. An iron bromide is first prepared, and this is decomposed by potassium carbonate. Some iron bromide is obtained in the manufacture of bromine, the vapours being absorbed by metallic iron, but most of it is made by mixing bromine and iron in such proportions that the compound  $\text{Fe}_2\text{Br}_3$  is obtained (*cf. Potassium iodide*). The solution of this bromide is filtered, and is run into a hot concentrated solution of potassium carbonate, until the reaction is exactly neutral or very faintly alkaline. 100 parts of iron bromide require from 56 to 60 parts of potassium carbonate, according to its purity. The solution is boiled for some time, to make the precipitate of hydrated iron oxides more dense; it is then separated from the latter by a filter or filter press, and is dried to complete dryness. The residue is dissolve behind the difficultly soluble potassium sulphate, &c., and is evaporated for crystallisation. Up to sp.gr. 1.53 this can be done at a boiling heat; the further evaporation should be done at a gentle heat, as with the iodide, to obtain hard crystals. The crystallisation takes place in stoneware or enamelled iron dishes. The mother-liquor can be freed from carbonate by cautious neutralisation with hydrobromic acid, and from sulphate by means of barium bromide. Any chloride present cannot very well be removed from the bromide; hence the bromine employed should be as free from chlorine as is required. Iodide can be removed by boiling with bromine. The last mother-liquors are best used up for the recovery of bromine. The German Pharmacopœia permits the presence of 2 p.c. KCl and 0.1 p.c.  $\text{K}_2\text{CO}_3$  in potassium bromide.

The drying of the potassium bromide takes place at 40° or 50°C., not above (to avoid decrepitation), on plates of stoneware or of sheet-iron covered with a very hard lacquer or with enamel.

The German manufacture of potassium bromide amounts to about 120 tons per annum, half of which is made at Schering's works at Berlin. A similar or larger quantity is made in America, and much more could be obtained if there were demand for it.

of potassium bromide is used in medicine and photography.

**Potassium iodide KI.** There are many ways for preparing this salt, but only the following processes are used for manufacturing purposes.

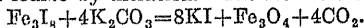
1. By  $\text{KIO}_3 + 6\text{HCl} \rightarrow 2\text{KCl} + 2\text{H}_2\text{O} + 3\text{Cl}_2$ . The reaction is,  $\text{KIO}_3 + 6\text{HCl} \rightarrow 2\text{KCl} + 2\text{H}_2\text{O} + 3\text{Cl}_2$ . The product is  $\text{KIO}_3$  which yields up its oxygen as  $\text{KIO}_3$  but as losses are caused by decrepitation and volatilisation, it is preferred to add some carbon in order to reduce the iodate.

The potassium hydroxide ought to be as pure as possible; most of the impurities of the

commercial product would enter into the iodide, and could not be removed from it by crystallisation, owing to the great solubility of the iodide. Hence it is preferable to start with the purest procurable potassium carbonate such as is supplied in the crystallised form to flint-glass makers, or that made by calcining potassium bicarbonate. The carbonate is causticised in the usual manner, employing pure lime, and iodine is introduced in small quantities into the boiling liquor until it has been exactly neutralised. The solution is evaporated to dryness, adding to it in the syrupy state some lampblack or charcoal, previously treated with hydrochloric acid and thoroughly washed with water, to the amount of  $\frac{1}{10}$  of the iodine present. The dry mass is gradually introduced into an iron pot, heated to redness, where it is brought to fusion, keeping the pot covered in order to prevent the iodide from volatilising. When completely fused, the mass is ladled out and is dissolved in water; the solution is filtered and is evaporated to about 1.82, when it crystallises on cooling. The evaporation is best performed by heating the solution in porcelain dishes on a sandbath, but not on the more concentrated liquors, to avoid the fire-end. A hood protects the operator from dust, draught, &c. In this way very good crystals are obtained.

The crystals, after draining, are dried on enamelled or lacquered iron plates in a current of hot air. If the salt is required to have an opaque appearance, the temperature is ultimately raised to 120° or 130°C.

2. *By means of iron.* A solution of ferrous iodide is prepared by digesting 3 parts of iodine with 1 part of iron borings and about 8 of water. The solution is filtered and one-third of the original quantity of iodine is dissolved in it with the aid of heat, so that it now contains a ferrous-ferrie iodide,  $\text{Fe}_3\text{I}_4$ . This solution is now mixed in a porcelain or enamelled iron vessel with a boiling solution of pure potassium carbonate, and the boiling is continued until the precipitate of ferrous-ferrie oxide has become dense, whereupon it is separated from the solution of potassium iodide by filtration. The reaction is:



The following modification, by Liebig, dispenses with the slow solution of iodine in ferrous iodide, and the troublesome frothing in the last reaction, owing to the escape of carbon dioxide. A solution is made of 12 parts iodine, 3 iron, and 32 water; to this is added, without previous filtration, a solution of 6 parts iodine in 12 parts caustic potash liquor of sp.gr. 1.345, and ultimately 9 parts of the same caustic liquor. The mixture is boiled for some time, filtered, evaporated to dryness, whereby a little ferric hydroxide is separated, re-dissolved, filtered and brought to crystallisation as above. The product is extremely pure, free from iodate, and the yield almost theoretical.

3. *By means of cuprous iodide.* Sometimes considerable quantities of cuprous iodide, containing from 60 to 66 p.c. of iodine, are shipped from Peru. This is converted into potassium iodide by washing it, suspending it in water acidified with a little sulphuric acid, passing in sulphuretted hydrogen until all the copper has been precipitated, adding enough solution of iodine in potassium iodide to destroy the excess

of  $\text{H}_2\text{S}$ , separating the solution of hydriodic acid (containing a little finely-divided sulphur) from the precipitate, and then adding potassium bicarbonate, which precipitates the sulphur which has now become globular, and bringing to crystallisation.

Nearly all the potassium iodide manufactured is employed in medicine and for photographic purposes. For the former purpose it is required to be entirely free from chloride.

Potassium sulphate  $\text{K}_2\text{SO}_4$  is obtained as a by-product in several manufactures which are described elsewhere; thus, in the working up of beet-root vinasse (*cf. Potassium carbonate*, p. 358), and in that of kelp, where it is separated as 'plate sulphate,' containing from 76-83 p.c.  $\text{K}_2\text{SO}_4$ , with 9-21 p.c.  $\text{Na}_2\text{SO}_4$ , some KCl and other salts (p. 350). It is also contained in the ashes of plants, and hence is present in commercial potashes; on purifying these it is obtained as a by-product, easily separable from the carbonate on account of the great difference in solubility.

The bulk of the potassium sulphate found in trade is, however, made either from kainite, or by the decomposition of potassium chloride with sulphuric acid.

Very large quantities of potassium sulphate are found at Stassfurt and Kalusz; not, however, in the isolated form, but principally in that of kainite  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , always mixed with sodium chloride, calcium sulphate, &c., so that commercial kainite contains at most 70 p.c. of the pure mineral. A very large number of processes have been invented for preparing potassium sulphate, either from kainite or from mixtures of magnesium sulphate (in the shape of kieserite) and potassium chloride or carnallite. In most cases an intermediate product is made, the  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

These minerals, and has received the name of 'kainite' or 'artificial schoenite.' From this sulphate is prepared with comparative facility, but at present it hardly pays to do so, at least in a sufficiently pure state for the manufacture of potassium carbonate; hence nearly all the latter is made from sulphate, obtained, with potassium chloride and sulphuric acid (*v. infra*), or from vinasse, while the schoenite is sold as a fertiliser.

We give here a short synopsis of the more important processes, which are described in detail in Pfeiffer's *Kali-Industrie* (Braunschweig, 1887), p. 349 *et seq.* The figures put in brackets are the numbers of the German patents.

1. *Preparation of artificial schoenite (kainite) from kainite.* Borsche and Brünjes (D. R. P. 10642, 11028, 10701, 12875, 17795) prepare a cold saturated solution of kainite and employ this for extracting fresh kainite at a temperature of 80°. The solution, which shows the sp.gr. 1.337, is clarified, and on cooling yields a crop of schoenite; the mother-liquors, which are rich in magnesium and sodium and potassium, are subsequently employed in the manufacture of potassium chloride from carnallite. This process is actually at work on a large scale.

Dupré and Hake (D. R. P. 6053) treat finely-ground kainite with a cold saturated solution of magnesium sulphate, at 20° or 25°C.; this carries away magnesium and sodium chloride, together

with one-third of the potash, two-thirds of the ... behind as schoenite. The dis- ... recovered. This process is ... on a very large scale; the employment of magnesium sulphate makes it rather more expensive than the preceding one.

H. and R. Grüneberg (D. R. PP. 10754, 18947) extract the kainite by a hot solution of schoenite or of sodium chloride; on cooling schoenite crystallises out.

Precht (D. R. PP. 10637, 13421, 19456) treats kainite with water or previous liquors at 120°-145°, under a steam-pressure of 2-7 atmospheres, with mechanical stirring, in a very ingeniously-constructed apparatus, which permits a mechanical separation of the double salt formed from the solution and from the residual rock-salt. The double salt formed in this way has the formula  $K_2SO_4 \cdot 2MgSO_4 \cdot H_2O$  and is converted into ... with a small quantity of water. This process is also at work on a large scale.

Similar processes are those of Lofasz (D. R. P. 29223) and Nahnsen (D. R. PP. 10772, 24744).

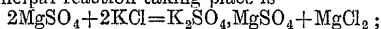
Dupré (D. R. P. 53237) works up mixtures of kainite and sylvinite ( $75KCl + 25NaCl$ ) by treating them with a hot solution of kainite, when almost pure  $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$  is obtained. The same inventor (D. R. P. ...) monia gas into a solution of kainite, separates the precipitated  $Mg(OH)_2$ , and again treats with ammonia, whereupon the whole of the potassium, in the case of pure kainite, crystallises out as  $K_2SO_4$ , or, if  $NaCl$  is present, as pure potassium-sodium sulphate,  $K_2Na(SO_4)_2$ . The ammonia is recovered from the last liquor by treating it with ... usually obtained.

Alkali Works (D. R. P. ...) ainite with the last mother-liquor from the manufacture of potassium chloride, containing 30 p.c.  $MgCl_2$ , thus producing various salts.

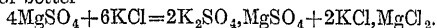
The schoenite thus obtained, which is entirely used for agricultural purposes, has the following average composition:

Potassium sulphate . . . . .	48-52 p.c.
Magnesium sulphate . . . . .	32-36 "
Water . . . . .	3-12 "
Sodium chloride . . . . .	1-5 "
Gypsum and insoluble matter . . . . .	0.2-5 "

Several processes for preparing schoenite from potassium chloride or carnallite and kieserite (Brünjes, D. R. P. 11; Ferber, D. R. P. 5068; Grüneberg, D. R. P. 5607; Westeregeln, D. R. P. 27404) need not be described here, because they do not seem to be profitable. The principal reaction taking place is



or better



Special processes for recovering schoenite from waste liquors are those of R. Grüneberg (D. R. P. 10753), Bernhardt (D. R. PP. 10821, 12493), Vorster and Grüneberg (D. R. P. 28772).

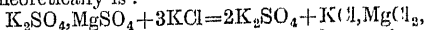
It is now a fixed rule of trade that 'crystallised' ... sulphate is to contain ... 48 or 50 p.c. real

2. Kul'schky (D. R. P. appl. K. 29803) makes use of the fact that a solution of mag-

nesium sulphate (kieserite), when appropriately diluted by water or  $KCl$  solution, on addition of solid  $KCl$ , at a temperature of 25°, does not yield schoenite, but at once a precipitate of potassium sulphate.

Saeger (D. R. P. 196500) describes a process for obtaining potassium sulphate from the mother-liquors of the manufacture of potassium chloride.

3. Preparation of potassium sulphate from schoenite. This can be done by simply running a saturated hot solution of schoenite upon dry powdered potassium chloride. The reaction theoretically is:—



but practically twice the theoretical quantity of schoenite must be taken, half of which remains in solution. The potassium chloride is rapidly changed into sulphate, and this is separated from the liquor by centrifugal force, taking care that the temperature does not fall below 40°. Below this temperature, first potassium chloride, then schoenite, and at last carnallite, crystallise out. The reaction can also be brought about by digesting crystallised schoenite with a cold saturated solution ... side, best of all in a set of ... combined with one another (Precht, D. R. P. 14534).

Schoenite, or a mixture of potassium chloride and magnesium sulphate, can also be converted into potassium sulphate by heat. Superheated steam (Sprenger, D. R. P. 27965) acts only very partially, but the addition of carbon (in the shape of small coal, brown coal, &c.) causes the reaction to proceed to its end by somewhat complete ... D. R. P. 15747; Leopold ... D. R. P. 31148). Townsend (D. R. PP. 10641, 29307) heats a mixture of potassium chloride, magnesium sulphate, and aluminium silicate in a muffle furnace in the presence of steam. This method has been further worked out by the Ascherslebener Werk, in 1885, and seems to be successful. Hans Müller ignites the mixture of  $KCl$  and  $MgSO_4$  with ferric oxide (D. R. P. 32325). Dupré and Hake produce, by means of lime or gypsum, a double sulphate of potassium and calcium, which is decomposed by igniting or by redissolving (D. R. P. 8021).

Nearly all the potassium sulphate made from schoenite, &c., is used ...

In all processes for ... magnesium sulphate (schoenite) or potassium sulphate, a great deal of trouble is caused by the large quantity of mother-liquor and the loss of potassium chloride from that cause. When this mother-liquor is boiled down, various salts are obtained which must be utilised as best possible, usually in the shape of fertiliser. Rubidium alum is also obtained from such mother-liquors.

4. Preparation of potassium sulphate by decomposing potassium chloride with sulphuric acid. This process, altogether analogous to the first stage of the Leblanc soda process, was first carried out by Messrs. Vorster and Grüneberg in 1863, near Cologne, and in 1868 at Stassfurt. About the same time (1864-1869) it was introduced in North Germany, France, and England. This way of producing potassium sulphate is nearly always employed when the product has to be converted into carbonate.

The raw materials are (1) potassium chloride of high strength of the Stassfurt manufacture, or,

as far as it goes, that from the working up of vinasse which already contains from 8 to 12 p.c. of sulphate, together with a little carbonate (p. 358). Coarse-grained salt is preferred to muddy or lumpy salt. (2) Sulphuric acid of sp.gr. 1.67, generally made at the same works. This is a lower strength than that preferred for decomposing sodium chloride, where the reaction is not so violent.

The decomposition of potassium chloride is so similar to that of sodium chloride that we can refer in most respects to the article SODIUM SALTS. The furnaces, acid-condensers, &c., are the same in both cases. We must, however, be careful in referring to the decomposition of potassium chloride.

The 'decomposing pans' (pots) are exactly similar to those used for common salt, so are the furnaces, of which all three descriptions, as employed for common salt, are in use here as well. But whilst in the case of sodium chloride the 'close,' or muffle furnaces are considered the best, owing to the better condensation of hydrochloric acid, many potash manufacturers prefer 'open'—that is, with a higher temperature but less condensation of acid. The decomposing potassium sulphate is done much more quickly in the 'open' pans, undoubtedly the best furnace for this work is Mactear's continuous revolving furnace as used at Kalk near Cologne.

The ordinary decomposing pans, which in England produce from 1500 to 2000 tons of salt cake before they are worn out, serve only for half or two-thirds of the work done with potassium chloride. They employ thin pans, 2½ ins. thick throughout, which last only for 250–500 tons of potassium sulphate. Blügel's fire-brick pans (D. R. P. 4207) do not seem to have answered.

The charges are from 5 to 10 cwt. of potassium chloride, and the corresponding quantity of sulphuric acid, which must be varied according to the varying strength of the chloride. The chloride coming from the vinasse works contains carbonate, which must be taken in account. With muffle furnaces the work is considered sufficiently good if 1 to 2 p.c. KCl and 2 to 3 p.c. 'free' SO<sub>3</sub> is left in the sulphate. Each charge takes about an hour to finish.

With reverberatory furnaces the undecomposed KCl is only 0.5 to 1.5 p.c.; the 'free' SO<sub>3</sub> 1 to 2 p.c.

With Mactear's furnace the Kalk works produce from 22½ to 25 tons of potassium sulphate in 24 hours; the product contains only 0.7 to 1.0 p.c. KCl, and as much free SO<sub>3</sub> (that is, bisulphate). The condensation of the hydrochloric acid is very good, 95 p.c. of the theoretical quantity being recovered.

Theoretically 100 parts K<sub>2</sub>SO<sub>4</sub> require 85.6 of pure KCl (corresponding to a yield of 116.8 of the former from 100 KCl), and 45.91 of SO<sub>3</sub> = 75.27 acid of sp.gr. 1.67; and the HCl escaping should be 41.84 parts = 133 parts hydrochloric acid of 32½ p.c. Practically with hand-furnaces 3.5 to 5 p.c., with mechanical furnaces 1 p.c., excess of sulphuric acid must be taken, or even more, if a minimum of undecomposed KCl has to be guaranteed.

The yield of sulphate is almost equal to theory, the small unavoidable loss being made

up by matter mechanically taken up from the furnace, flue-dust, &c. The quality has been mentioned above.

The following is an analysis of good commercial sulphate made from 98 p.c. potassium chloride:

K <sub>2</sub> SO <sub>4</sub> . . . . .	95.00 p.c.	SO <sub>3</sub> H <sub>2</sub> . . . . .	1.84 p.c.
Na <sub>2</sub> SO <sub>4</sub> . . . . .	0.50 "	CaO, Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.81 "
KCl . . . . .	1.50 "	Insoluble . . . . .	0.35 "

The yield of hydrochloric acid is usually only 70–75 p.c. of the theoretical one with reverberatory furnaces, 90 p.c. and upwards with muffle furnaces or the Jones and Walsh furnace, 95 p.c. with Mactear's continuous furnace.

The wages per ton of sulphate are from 6.5 to 7.2 marks (including the condensation of hydrochloric acid) for hand furnaces, but only one-half or even less for Mactear's furnace.

The fuel used amounts to 9 cwt. of good Westphalian coal with muffle furnaces, or 4–5 cwt. coke and 3 cwt. coal for reverberatory furnaces. With Mactear furnaces there is no saving of fuel, since it is necessary to provide steam for the engine turning the furnace.

Potassium aluminium sulphate (*Potash alum*) (cf. ALUM).

Potassium carbonate. Impure potassium carbonate, commercial 'pot-ashes,' has been known from very ancient times. Aristotle mentions its preparation by the incineration of rushes, Dioscorides by that of argol. Kunkel, in the seventeenth century of our era, proved the identity of these two products. The Romans employed them in medicine and for soap-making; the latter is even now the most important outlet for that article, as soft soap cannot be made with soda. Otherwise soda tends more and more to displace the more expensive potash, and has done so in the manufacture of hard soap, in that of glass (partially even in that of flint glass and Bohemian crystal), and more recently, to some extent, even in some manufactures which formerly seemed to be only possible with the use of potash, as that of chromates, chlorates, and ferrocyanides. In the manufacture of oxalic acid from sawdust caustic potash is also considered indispensable.

Leaving aside such methods as cannot be classed among manufacturing processes (such as the incineration of argol or wine-lees) with or without potassium nitrate, we may enumerate the following commercial sources of potassium carbonate:—

1. *Mineral.* (a) From potassium chloride and sulphate by Leblanc's or other processes.

(b) From feldspar and other rocks containing potash.

2. *Vegetable.* (a) From wood ashes.

(b) From beet-root molasses (vinasse).

(c) From kelp or varec (very unimportant).

3. *Animal.* From the 'suint' of sheep's wool.

Potassium carbonate (or caustic potash) manufactured from the chloride or sulphate. All processes starting from this base are of very recent date, and only that imitating the Leblanc soda process has acquired great importance. In 1861 Messrs. Vorster and Grüneberg, of Kalk, near Cologne, commenced working up potassium sulphate (which at that period was a by-product in working up vinasse cinder, less valuable than

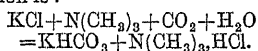


chloride, and difficult to get rid of) by the Leblanc process, and this industry has gradually spread over other parts of Germany, which is the principal seat of that industry. In England the Leblanc process seems to have been attempted with potash about 1863 or 1864, but it was only somewhat later employed for making commercial carbonate, and has not gained any great extension there. In France it was introduced in 1873, at Croix, near Lille, and at other works in the North.

We shall now enumerate the principal processes for manufacturing potassium carbonate from chloride or sulphate, omitting those which have been originally proposed for soda without special adaptation to potash.

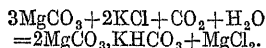
(1) *From chloride, without passing through sulphate.* The ammonia process, which is of such importance for the manufacture of soda, is not applicable to potash, because the solubility of potassium bicarbonate is too great. An attempt to overcome this by working in an alcoholic solution, by Groussilliers (D. R. P. 10552), was entirely unsuccessful.

A very ingenious process is that of Ortlieb (D. R. PP. 5706, 9376, 13397), replacing ammonia by trimethylamine, which is obtained by a certain treatment of beet-root vinasse (cf. below). The great solubility of trimethylamine hydrochloride admits of separating the potassium bicarbonate; cold, pressure and agitation promote this object. The reaction is:—



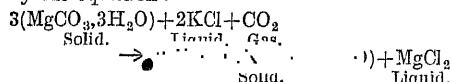
The limited supply of the reagent, its high price, its extremely *volatile* nature are drawbacks to this process. It seems to have worked well in the experimental factory at Croix, where it was, however, given up after a short time.

The *ammonia* process (D. R. P. 152) is also applicable to natural magnesias, or to magnesias in chloride, and passing in carbon dioxide under pressure, when a double carbonate of potassium and magnesium is precipitated, which can be decomposed into the single salts by heating or dissolving in water:



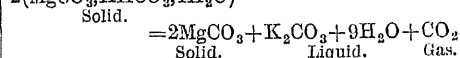
The recovery of magnesia from the chloride would have presented difficulties, but there must have been others as well, for the works started at Stassfurt were soon stopped. Delsol (D. R. P. 39903) patented an addition to Engel's process.

The magnesia-potash process has been worked out more successfully in another shape, principally by Precht, and is now carried out on a large scale. This process starts from the fact that the double magnesium carbonate, treated with *hydrochloric acid*, forms  $\text{MgCl}_2$  and solid magnesium carbonate, and that the latter can be transferred into solid magnesium carbonate and a solution of potassium carbonate. The first and principal part of the process is represented by the equation:



One-kiln gases (30-35 p.c.  $\text{CO}_2$ ) are passed

into a solution, saturated at 20°, of strong potassium chloride (95-97 p.c.), made into a paste with tri-hydrated magnesium carbonate with application of a series of vessels and mechanical agitation. The solid double salt formed is separated by suction from the mother-liquor, and is washed with a solution of  $\text{MgCO}_3$ , until it contains no more than 0.1 or 0.2 p.c. Cl. The mother-liquor contains a large quantity of  $\text{MgCO}_3$ , and is used in various ways. The solid potassium magnesium carbonate is D. R. P. 50786 of the *Continental*, which consists in heating it under pressure in agitating boilers to 140°, which produces the reaction:



The  $\text{MgCO}_3$  formed is anhydrous and reacts too slowly to be re-employed in the first stage; it is either sold as such or converted into anhydrous  $\text{MgO}$  by calcining. Modifications are described in D. R. PP. 55182, 125987, 143408, 143595, 143409, 141408, 141408, 143594, 144742, 155007, 172313.

According to D. R. P. 143409, the potassium magnesium carbonate is decomposed by water at 80°, yielding  $\text{K}_2\text{CO}_3$  and a crystalline form of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , which is used over again.

A third process is described in D. R. P. 172313. The potassium-magnesium carbonate, stirred up in water, is decomposed at 40° by magnesia (hydrated or anhydrous), yielding solid  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  and a solution of  $\text{K}_2\text{CO}_3$ .

Sometimes the first process is combined with the second or third, commencing the decomposition by the latter and finishing it by the first. Another modification is described in D. R. P. 135329 of the Deutsche Solvaywerke, 157354, 188504.

In 1885, Borsche and Brünjes patented the production of carbonate from chloride or sulphate by means of ammonium-magnesium carbonate and carbon dioxide.

Wittjen and Cuno (D. R. P. 19197) employ zinc compounds in the production of magnesium compounds for a

Scheele's process, treating an alkaline chloride with *litharge*, has been repeatedly attempted without practical success. It has been applied to potash by the Société anonyme Lorraine industrielle (D. R. P. 23701), and by D. C. Knab.

Gilchrist Thomas (D. R. P. 30209) treats alkaline chlorides in the shape of blocks in a heated converter with *pig iron*, containing little carbon, but upwards of 4 p.c. silicon, in a stream of hot air and superheated steam.

Another proposed precipitating *acid*, and decomposing the potassium fluosilicate by lime.

Several inventors utilise the slight solubility of potassium *bisulphate* (Goldenberg) and *vinocalate*. Bohlitz decomposes the latter by magnesium carbonate. None of these processes is

of alkaline chlorides by the *galvanic current* has been frequently attempted. This process has been applied to carnallite by Wollheim (D. R. P. 16126); at Aschersleben it was to be tried on a large scale with machines of 120 h.-p. The Griesheim Chemical

Company at Frankfort have carried out the electrolytical manufacture of caustic potash and chlorine from strong potassium chloride with great success, and on a very large scale, for some years past, but it is not known by what special process.

(2) *From sulphate.* Leblanc's process will be described below. It has been extended to a direct treatment of *schoenite* by Vorster and Grüneberg, and Precht (in 1885) even patented a direct addition of magnesium sulphate to the potassium sulphate employed for that process. Clemm (1863) and Precht (1858) decompose *schoenite* by heating with *coal*, whereupon a mixture of magnesia and potassium sulphide is formed, which is treated with moist carbon dioxide.

Of the processes in which compounds of barium, strontium, aluminium, &c., also aluminium phosphate, are employed for decomposing alkaline sulphates, we mention only the process of Jannasch (D. R. P. 51224), in which potassium sulphate, obtained by a special process from kainite, is boiled with finely ground native barium carbonate (witherite). As the native mineral and no carbonic acid are employed, the decomposition is sure to be incomplete.

E. Pfeiffer states (Zeitsch. f. Chem. 8, 1338, 1375) that he decomposed, for some time, potassium sulphate with barium carbonate on a large scale. W. Bramley has patented the same process in a slightly modified form (1050, 1886).

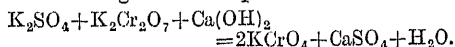
Dupré (D. R. P. 47037) mixes solutions, saturated at 0°, of potassium sulphate and sodium carbonate, containing 85 grams  $\text{Na}_2\text{CO}_3$  and 139 grams  $\text{K}_2\text{SO}_4$  per litre), and cools down very cautiously below 0°, passing a stream of  $\text{CO}_2$  into the liquid; or else 140 grams sodium bicarbonate + 140 grams potassium sulphate, dissolved in 1 litre water, are cooled down to -6°, when 200 grams of Glauber's salts crystallise out, which are separated from the solution of potassium bicarbonate by a centrifugal machine. At -10° the separation of Glauber's salts is more complete, but then the process is interfered with by the formation of cryohydrates. A further patent (D. R. P. 52163) contains important improvements of the process.

Vogt and Figge (D. R. P. 31675) convert alkaline sulphates into a porous form by mixing them with silica, clay, magnesia, or lime, calcining, and moulding into small pieces. These are introduced into upright iron cylinders, in which the sulphate is first converted into sulphide by the action of carbon monoxide at a bright-red heat, carbon dioxide being given off, and then into carbonate by the action of carbon dioxide and steam at a lower temperature. These cylinders are combined to a set, into which carbon monoxide is passed at one end and hydrogen sulphide passes out at the other end. The cylinders are discharged from the bottom; the mass is lixiviated, and the porous substance employed over again. This process was to be tried on a large scale at the Aschersleben works; it does not seem to have been successful.

Kaysor (Amer. Pat. 320256) converts alkaline sulphates into carbonates by a mixture of equal

volumes of  $\text{CO}_2$  and CO at a low red heat;  $\text{SO}_2$  escapes, and is utilised for converting chloride into sulphate.

Römer (D. R. PP. 66533, 67320, 67780) dissolves potassium sulphate (or *schoenite*) and potassium dichromate in water at 60° or 80° and neutralises exactly with milk of lime, whereby the following reaction is produced:



The precipitated gypsum is removed by filtration, the remainder of it by precipitation with potassium carbonate, or by evaporation *in vacuo* at 80°. The solution of potassium dichromate is concentrated by boiling down and treated with  $\text{CO}_2$ , whereby potassium dichromate and bicarbonate are produced. The former is precipitated by  $\text{KHCO}_3$  remains in solution. The solution is cooled to 45°-50° Bé.,  $\text{CO}_2$  escapes and  $\text{K}_2\text{CO}_3$  is obtained.

At the Buckau Chemical Works (Fischer's Jahresb. 1894, 469), kainite is treated with sulphuric acid, the escaping HCl being condensed. The solution is treated with milk of lime, separated from the lime, and treated with barium sulphide. After removing the barium sulphate, the solution of sulphides is decomposed by carbon dioxide (converting the  $\text{H}_2\text{S}$  given off into sulphuric acid); the alkalis are converted into bicarbonates and the sodium bicarbonate crystallises out on cooling, leaving potassium bicarbonate in solution.

#### *Potassium carbonate by the Leblanc process.*

This process consists in fusing potassium sulphate with calcium carbonate and coal. Both the theory and the practical execution of this process are exactly like its original application to soda, to which we must refer for particulars. This also holds good for the apparatus, boiling-down pan, &c. We here point out only those matters in which the potash process differs from the soda process.

The potassium sulphate is nearly always that obtained by the reaction of potassium chloride with sulphuric acid. *Schoenite* obtained from *schoenite* is too light, and is easily carried away by the draught. Without damaging the process, some *schoenite* may be mixed with the  $\text{K}_2\text{SO}_4$ .

The furnaces are almost exactly like black-ash furnaces; the only difference is that the hearth is made a little "dished"—that is, with a depression of 2 ins. in the centre—to counteract the tendency of the melting mass to penetrate into the hearth and raise it up.

The usual mixture is: 100 potassium sulphate, 80 to 90 limestone, and 40 to 50 coal; but on starting a new furnace the proportion of limestone and coal is somewhat increased until the furnace has attained its full heat. Small batches (of 2½ to 3 cwt. sulphate) are finished in 40 to 50 minutes, large batches (up to 5 cwt. sulphate) in about 75 minutes, so that there is no advantage with the latter; on the contrary, small batches are more easily worked, and the furnace suffers less; there is also less volatilisation of potassium carbonate. Usually thirty batches of 3 cwt., or 2½ cwt., of sulphate are turned out.

Towards the end of the operation the fusing mass becomes thinner than with soda; the end

of the operation is at hand when the evolution of 'candles' begins to diminish slightly, whereupon the batch must be drawn out at once. The temperature rises from 700° at the beginning to 900°C. at the end.

Good black ash from potash should contain 40 to 45 p.c. potassium carbonate (counting the hydroxide as such), and not above 0.5 to 1.5 undecomposed sulphate, and 0.5 to at most 1.0 sulphide. The less limestone and coal are used in the first stage the less caustic it contains. Cyanide is formed from the nitrogen of the coal, sometimes to such an extent that the recovery of ferrocyanide is a paying process. German coal yields less cyanide than English (Newcastle) coal.

100 parts of potassium sulphate, with an average proportion of limestone, yield from 157 to 163 parts of black ash.

The black ash is left to cool for 1 or 2 days, and is broken up in smaller pieces than with soda (say, not above 4 ins. diameter). The lixiviation takes place precisely as with soda. For each ton of black ash to be lixiviated in 24 hours there should be vat space amounting to from 250 to 350 cubic feet. The water is used in summer without heating; in winter about 30°C.; the 'strong vat' should be about 40° to 45°C. The strong liquor, as it is run off, tests from 36° to 60°Tw.; the average is 42°Tw. It is greenish-yellow, sometimes with a reddish cast. It contains all the same impurities as soda tank-liquor. Pfeiffer quotes the following quantities found in two samples, calculated upon 100 parts of  $K_2CO_3$  (+KOH):

Potassium sulphate	<sup>a</sup> 3.27	<sup>b</sup> 4.34	parts
" sulphide	3.17	2.35	"
" thiosulphate	1.72	3.61	"
" silicate	1.98	2.24	"
Total sulphur (as $K_2SO_4$ )	9.6	11.36	"

There is also aluminate, ferrocyanide, ferrosulphide, &c. The tank-waste ought not to contain above 0.2 to 0.3 p.c. of soluble potassium carbonate.

By directly evaporating the tank-liquor to dryness, and calcining, a yellow or reddish potash is obtained which must be purified by redissolving, bringing again to dryness, and calcining. It is decidedly preferable to carbonate the tank-liquors exactly as is done with soda liquors, whereby the hydroxide and sulphide are converted into carbonate, and the ferrous sulphide into ferrous carbonate. This can be done by gaseous carbon dioxide in the manner described for soda, or very advantageously by means of potassium bicarbonate.

The evaporation of the liquor takes place in pans heated by the waste fire of the black-ash furnace either from the top or the bottom. Pans fired from the top suffer less, and the evaporation takes place more quickly than with bottom heat, which requires about twice the heating surface; still, bottom-fired pans are generally preferred in potash works, because the liquors are less contaminated with  $SO_2$ , soot, coal-ashes, &c.

The evaporation can be carried on with good liquors to 77°Tw. before any sulphate 'salts out.' At this point the liquor is run off into coolers, where most of the sulphate is precipitated in a muddy form, together with a little  $K_2CO_3 \cdot 2H_2O$ . With inferior liquors, containing much sulphate,

the sulphate may 'salt out' even at 60°Tw., and this takes place in any case above 77°Tw. up to 123°Tw., at which point all the sulphate will have been removed. That part which is precipitated in the pans during evaporation would, in bottom-fired pans, produce very inconvenient crusts unless it were constantly removed by 'raking.' This can be done most conveniently by hand, or by Thelen's mechanical fishing-pans. In the case of top-fired pans such deposits are harmless, and hence at some works they employ bottom-heat up to 77°Tw., and top-heat above that point.

The potassium sulphate, precipitated both in the pans and by cooling the liquor, is drained, freed from adhering liquor by cold water, and used over again in the black-ash furnace; this is an advantage over the Leblanc soda process, where the sulphate remains with the soda-ash, and is thus lost. When using coal containing much nitrogen it pays to extract the potassium ferrocyanide, which is found together with the sulphate. The deposit is for this purpose dissolved by water and steam to sp.gr. 66½°Tw.; the solution is clarified and run into coolers, where the ferrocyanide crystallises out. It is purified by re-dissolving to 60°Tw. The yield is generally below 1 p.c. of the carbonate.

The finishing operation takes place in a calcining furnace, similar to those employed for soda, but always connected with a cast-iron pot or a wrought-iron pan, set at the end opposite the fireplace, for utilising the waste heat. In those pans the liquor is brought to at least 123°Tw., and sometimes to the state of paste. In the latter case the furnace-bed is made level; when intended for liquor of 123°Tw. it must be made to slope down from the working-door to a depth of 5 or 6 inches. In any case the furnace must be brought to a bright-red heat before charging it with fresh liquor or paste, so that a crust is formed at once on the bottom, and there is less tendency for the liquor to penetrate into the furnace-bed, which, of course, must be made with the greatest care, exactly like that of a black-ash furnace. The new crusts forming at the surface must be worked down, and when the whole mass is dry it must be detached from the brickwork and broken up by means of the 'rake' and the 'paddle.' In the intervals of working the mass the heat is raised by closing the door and stirring the fire until the surface shows just incipient fusion, but not above this point. When the mass has been brought to a uniform powder, it is drawn out and is left to cool on an iron plate. With liquor of 123°Tw., four or five batches of 5 or 6 cwt. of potash can be turned out in 24 hours. It is important to avoid any interruptions of work, which nearly always produce cracks in the brickwork.

With carbonated liquors a single calcination furnishes a marketable product containing 85 to 92 p.c. carbonate, 10 to 2 sulphate, 2.5 to 0.5 chloride, and a little insoluble matter. This is, however, frequently refined by redissolving it with the aid of steam, in tanks provided with a suspended sieve or with a mechanical stirrer, to a strength of 110° or 112°Tw., and allowing it to settle, when, on cooling, most of the sulphate crystallises out. The clear liquor is further concentrated to 123°Tw. in the pans behind

the calcining furnaces, and is calcined with special care. This refined product contains:

Potassium carbonate (hydroxide, silicate, aluminate)	} from 92 to 98.5 p.c.	
Sodium carbonate	2.5	0.5
Potassium chloride	2.5	0.6
Potassium sulphate	3.0	0.4

The quantity of silicate and aluminate is very slight. Phosphate, which always occurs in potash from vegetable sources, is absent here.

*Hydrated potassium carbonate.* For some purposes, especially for flint-glass making, potash entirely free from sulphate, but containing 12 to 18 p.c. of water, is used.

Ordinary carbonate is dissolved to a strength of 142°Tw., or even above this; the solution is allowed to cool and settle, which causes nearly all the sulphate to separate. The clear liquor is evaporated in flat-bottomed pans to the state of a thick paste; the fire is now drawn, and the mass is constantly stirred till it has been converted into a coarse powder. It is less deliquescent than calcined potashes; its composition approaches the formula  $K_2CO_3 \cdot 2H_2O$ .

3. *Potash from felspar and other rocks.* The recovery of potash from rocks containing it in large quantities (sometimes up to 14 p.c.  $K_2O$ ), which potash by their decomposition have

potash existing in the soil, and hence indirectly that obtained from them, have been attempted many years past without much success. The most promising process seemed to be that of Ward and Wynants, in which finely-ground felspar (orthoclase) is ignited with lime and fluorspar until the mass had fritted. On lixiviation potassium hydroxide and silicate are decomposed by means of carbon dioxide. The silicate is removed, and potassium carbonate can be obtained in a very pure form. Both this and all similar processes are quite out of the field, since the discovery of the Stassfurt deposits has opened out an incomparably more convenient source of potash, which is, at any rate, sufficient for hundreds of years to come. The proposal of Spiller (J. Soc. Chem. Ind. 1882, 128), to heat felspar with calcium fluoride and sulphuric acid in order to obtain potassium and aluminium sulphate, has very little prospect of practical realisation.

E. Hart (U.S. Pat. 997671) prepares potassium sulphate from potassium-bearing rocks by fusing them with barium sulphide so as to give a glass, and extracting the potassium from the powdered product by a mineral acid. Potassium alum, for instance, is obtained by fusing 1 mol. orthoclase with 1 mol. barium sulphate and 2 at. coal and treating the product with sulphuric acid.

Thompson (U.S. Pat. 995105) mixes finely ground felspar with an alkaline acid sulphate and chlorides, say, 5 felspar, 5 acid sodium sulphate and 1.8 sodium chloride, keeps the mixture at a red heat for 2 or 3 hours, grinds it after cooling, lixiviates and allows the solution to crystallise. The acid sulphate, acting on the chlorides, liberates hydrogen chloride, which at the high temperatures acts upon the felspar with formation of potassium chloride; this, with the  $NaHSO_4$ , forms again  $HCl$  and  $K_2SO_4$ . In this

way, he asserts, 80 to 90 p.c. of the potassium contained in felspar is recovered as sulphate.

Herstein (J. Ind. Eng. Chem. 1911, 426) fuses felspar with calcium chloride and a like quantity of calcium carbonate in revolving furnaces; potassium chloride escapes in the state of vapour, while cement clinker remains behind.

4. *Potash from wood-ashes.* This was formerly the only source of potassium carbonate on a large scale. About the middle of the last century it lost much of its importance through the rise of the vinasse industry; and, since the manufacture of potassium carbonate by Leblanc's process has more and more extended, that made from wood-ashes has correspondingly receded into the background. Nor is this result very much to be deplored, for the ready sale formerly of potassium carbonate on a large scale. About the middle of the last century it lost much of its importance through the rise of the vinasse industry; and, since the manufacture of potassium carbonate by Leblanc's process has more and more extended, that made from wood-ashes has correspondingly receded into the background. Nor is this result very much to be deplored, for the ready sale formerly obtained for potash from wood-ashes led to the devastation of forests at an alarming rate. On the other hand, it is a fact that in some localities the only use to be made of timber is its conversion into ashes, and extraction of potash therefrom; but the places where this can be called in any way a rational process are getting more and more scarce. Several of the brands formerly found in trade have become extinct. Since the use of wood as fuel has also very much diminished during the last generation the collecting of ashes from this source, which were formerly sold to the potash manufacturers, is now too troublesome in most countries, and such wood-ashes are there only used for domestic and agricultural purposes. Only some parts of Russia, Transylvania, Illyria, Canada, and the United States, still continue to furnish supplies of commercial pot-ashes (pearl-ash, &c.).

Potash is an indispensable element for the growth of most plants, and hence is found in their ashes. But where it is associated with much silica and phosphoric acid the ashes contain but little carbonate, and are not available for the manufacture of potash. This, for instance, holds good of straw-ash. The only practically important source of potash is *wood-ash*; it is true that the ashes of several herbaceous plants contain a great deal more of potassium carbonate than the ordinary woods, and it has been actually proposed to grow such herbs for this manufacture; but this is irrational and without any hope of success, as these quickly exhaust the soil much more than the woods can be made up by the natural growth of the minerals composing it.

The following table shows the percentage of potassium in some of the more important woods and plants:—

	Ash per cent.	Potash per cent.
Pine wood	0.34	0.045
Poplar wood	—	0.075
Beech wood	0.58	0.145
Beech bark	—	0.153
Ash wood	1.22	0.074
Oak wood	1.35	0.153
Oak bark	—	0.420
Rox wood	—	0.226
Willow wood	2.80	0.285
Elm wood	2.55	0.390
Vines	3.40	0.550
Thistles	—	0.500
Rush	—	0.508

	Ash. per cent.	Potash per cent.
Ferns . . . . .	3.64	0.626
Nettles . . . . .	—	2.503
Vetch . . . . .	—	2.750
Wormwood . . . . .	—	7.300

In Canada most potash is made from elm, birch, larch, and maple.

The potash is contained in these plants in the shape of sulphate, chloride, silicate, and organic salts. The latter, on calcining, are converted into carbonate, part of which may be converted into hydroxide on lixiviation if lime is present; any silica present will pass into potassium silicate, and this renders the manufacture of potash from straw quite irrational. Where soda is present in large quantities the potash obtained must also be of inferior value. Hence the quality of potash found in trade is very varying, quite apart from actual falsifications with coal-ashes, soda, &c.

The manufacture of commercial potash is a very crude process. The wood is burned in pits dug in the earth in places sheltered from wind. The collected ash (beech-wood ash is preferred to all other wood-ashes; vine stalks, ferns, &c., where obtainable in quantity, are still better) is spread on a stone floor, sprinkled with water, and worked through until it is evenly damp. Sometimes (in Canada) a little lime is mixed with it, which afterwards causes the formation of caustic potash. The damp ash is placed in casks provided with a false bottom, covered with straw, and water (preferably hot) is poured over it. After some time the liquor thus formed is drawn off by a plug-hole at the bottom; if it is about 32°Tw. strong it can be boiled down at once; the weaker liquors and washings are used for lixiviating fresh ash. The residue, which with this rough style of working still contains much potash, is a good manure.

The boiling-down is also generally a very rough process. In lieu of pans possessing a large heating-surface (pans fired from the top would be the best) usually circular cast-iron pots fired from below are employed, in which the liquor is boiled down to dryness. In spite of stirring up the mass before it becomes quite dry much of it burns fast to the pot, causing a great waste of fuel and a speedy destruction of the pot. In America the mass is heated nearly to redness, and is converted into greyish-pink compact 'pot-ashes,' which are assorted by official inspectors into 'firsts,' 'seconds,' 'thirds,' and 'unbrandables.' The brown crude pot-ashes are calcined in reverberatory furnaces, which causes the carbonaceous and other organic matter to burn away, the hydroxide to be carbonated and the sulphide, &c., to be converted into sulphate. An excess of heat has to be avoided, because the mass would then fuse, and this would prevent the organic substance from being burned. The resulting product should be white or blueish—the latter from potassium manganate. A purer product is obtained by dissolving the product of calcination in water, separating the liquor from the insoluble substances, evaporating and calcining again; the American 'pearl-ashes' are thus made.

The common American 'pot-ashes' are frequently made with addition of, so much lime that they contain the major portion of the pot-

ash in the caustic state; thus some of the silicate is also recovered which would be lost otherwise. This potash fuses below a red heat; it is therefore only boiled down until the mass solidifies on

cooling. The potash must be even more pure than the soda, to resist atmospheric moisture. The natural mineral potassium carbonate, although this is also deliquescent. Such caustic potash is very much in request by soap makers; it takes less lime in making their lye, and causes less loss, just in proportion to the smaller amount of lime-mud.

'Purified carbonate of potash' is made from ordinary carbonate in two different ways. In one the carbonate is stirred up in an iron pot with  $\frac{1}{2}$  or 2 times its weight of cold water, and the mixture which gets hot allowed to cool down before siphoning off the clear liquor. The sulphate and some chloride remain behind, together with the insoluble matter; the residue is not washed (which would cause the sulphate to be re-dissolved), but only pressed. The liquor, containing mostly carbonate, but also chloride and silicate, is brought to dryness, stirring it up to the end. In the other the solution is made with hot water, the residue is exhausted in the same way, the liquors are boiled down to sp.gr. 1.50 and allowed to cool, when the sulphate and some chloride crystallise out. This process is more expensive than the former. In order to make still purer carbonate for flint-glass manufacture, pearl-ashes are calcined with a little sawdust, lixiviated, the clear liquor is boiled down and calcined, and this is repeated twice over; the last product is dried down until it is converted into granular 'crystallised' carbonate with 15 to 18 p.c. of water.

According to Chem. Zeit. Rep., 1908, 3, potashes are manufactured from the stems of sunflowers in 24 factories in Northern Caucasia, to the extent of 100,000 to 120,000 tons per annum.

The potash from bamboo-cane, made in British Burmah (Romanis, Chem. News, 45, 158), testing 32.54  $K_2O$ , 0.98  $Na_2O$ , 18.72  $KCl$ , 16.95  $SiO_2$ , 8.07  $CO_2$ , 2.71  $SO_3$ , 1.10  $Al_2O_3$  and  $Fe_2O_3$ , 19.43  $H_2O$ , partakes more of the nature of a silicate than that of a carbonate (like all other potashes made from woody plants).

The quantity of wood potash in the whole world was estimated by H. Grüneberg, in 1873, at 20,000 tons per annum. Even then its production had very much receded in comparison with former times. The exportation from Russia, formerly the leading country in that respect, which in 1864 had been 11,000 tons, in 1873 had declined to 5540 tons; New York, which in 1865 exported 2610 tons, in 1873 only exported 388 tons. Of the American exportation, about one-tenth is pearl-ashes, nine-tenths caustic pot-ashes. At present the total quantity of wood potash annually produced cannot exceed 10,000, or at most 15,000 tons; a great part of this is consumed in the countries where it is produced.

5. *Potash from beet-root vinasse.* In the last stage of the manufacture of sugar from beet-root a syrupy liquid is obtained, which, although containing a very large quantity of sugar, cannot be brought to crystallisation, owing partly to the presence of organic impurities, but chiefly to

## ANALYSES OF COMMERCIAL POTASHES, PEARL-ASHES, &amp;C., FROM WOOD.

Origin	Quality	K <sub>2</sub> CO <sub>3</sub>	KOH	Total available alkali calc. as K <sub>2</sub> CO <sub>3</sub>	Available potash calc. as K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> SO <sub>4</sub>	KCl	Analyst
American potash	—	68	—	75.5	68	5.8	15.3	8.1	Pesier
" "	1	41.7	49.6	108.2	106.4	1.4	4.0	2.0	F. Mayer
" "	2	19.4	44.4	87.8	77.2	8.2	16.1	5.6	
" "	2	18.3	36.6	81.7	65.9	12.2	15.1	14.6	Grüneberg
" "	2	34.5	29.6	81.8	77.9	3.0	15.0	7.5	
Montreal potash	firsts	43.87—	50.03—	92.49—	88.83—	6.24—	16.07—	4.41—	Tatlock
		26.16	36.50	89.82	85.54	2.84	10.40	1.68	
	seconds	38.53—	42.44—	85.79—	76.24—	11.47—	18.92—	12.82—	
		21.71	30.63	85.08	73.98	8.52	9.18	6.13	
Canadian pearl-ashes	thirds	46.31	6.14	72.10	53.86	17.81	20.53	7.63	Pesier
	—	71.3	—	74.2	71.3	2.3	14.8	3.6	
" "	—	65.0	—	70.2	65.0	4.0	21.0	7.0	Grüneberg
" "	1	77.50	—	80.98	77.50	2.86	11.65	2.65	Tatlock
" "	—	71.38	—	74.53	71.38	2.31	14.38	3.64	
Tuscan potashes	—	74.1	—	78.0	74.1	3.0	13.4	0.9	Pesier
" "	—	62.6	—	76.9	62.6	11.0	15.5	4.5	Grüneberg
Illyrian potashes	1	89.3	—	89.3	89.3	0.0	1.2	9.5	
Hungarian "	3	44.6	—	68.0	44.6	18.1	30.0	7.3	
Galician "	—	46.9	—	51.6	46.9	3.6	20.9	11.1	
Russian "	—	69.61	—	73.77	69.61	3.09	14.11	2.09	Pesier
" "	—	50.84	—	66.78	50.84	12.14	17.44	5.80	Bastelaer

the large quantity of salts present. The latter circumstance prevents the utilisation of such 'beet-root molasses' in a similar way to cane-sugar molasses. For a long time the only way of dealing with beet-root molasses was this: diluting them with water, neutralising their alkaline reaction with sulphuric acid, causing the liquor to enter into alcoholic fermentation by means of yeast, and distilling off the spirit (which is of rather inferior quality). The liquor remaining behind in the stills, called 'vinasse' in French or 'schlempe' in German, was formerly always led back upon the fields on which the sugar-beet had been grown. To some extent this is still done; nor can it be denied that this is, after all, the simplest and at the same time the most rational way of dealing with it, wherever carriage is practicable, for in this way the mineral substances (especially potash and phosphoric acid) taken from the soil in the shape of beet-root crops, are given back to it in a soluble form, together with the nitrates formed in the plants, which are lost in every other process of utilising the vinasse.

On the other hand, the large quantity of potash contained in this liquor has, under ordinary circumstances, a greater commercial value, even deducting the expense of recovering it in the shape of potassium carbonate, than in that of liquid manure. This was pointed out about 1830 by Dubrunfaut, to whom is due the introduction of the very important industry of beet-root potash, which, however, did not take firm root until about 1850, first in the north of France, and then in Belgium and Germany. In France this still forms the most usual way of dealing with molasses, whilst in Germany it has become more usual to extract the sugar by means of the osmose, the strontia, and the lime processes. The strontia process easily admits of recovering the potash in the shape of 'vinasse cinder'; but the dilute liquids, obtained by the osmose and the lime process, are usually only applied for manuring the fields. Pfeiffer (Kali Industrie, 101) estimates the potash contained in the beet-root-juice worked in Germany in 1883,

calculated as 80 p.c. potassium chloride; at 15,000 tons, 8000 tons of which was rendered back to the fields by the factories working the osmose and substitution processes, whilst 7000 tons passed into molasses. Of the latter, about 1350 tons were recovered in the shape of 'schlempekohle' from the strontia process, and 3000 or 4000 tons from the factories working the molasses for spirit. In France sometimes the osmose liquor is worked for: . . . . . which forms 50 p.c. of the . . . . . boiling down the liquor to 40° Bé. (Dingl. poly. J. 245, 192; 264, 510).

Sugar-beet may be said to yield about 1 p.c. of ash, nearly half of which consists of potash (calculated as K<sub>2</sub>O), present in the juice to a great extent in the shape of nitrate and of salts of organic acids, all of which on calcining yield carbonate. Very little of it goes away with the sugar: nearly all remains in the molasses, which contain from 44 to 50 p.c. of sugar, 14 to 18 p.c. other organic substances, 16 to 18 p.c. salts, and 15 to 18 p.c. water; the ash amounts to 10 to 12 p.c. The ash is composed as follows, according to Kroecker:

	Soluble	Insoluble
Potash . . . . .	47.88	1.70
Soda . . . . .	2.34	0.17
Lime . . . . .	—	5.08
Sodium chloride . . . . .	12.92	—
Sulphur dioxide . . . . .	1.53	—
Carbon dioxide . . . . .	22.39	4.00
Silica . . . . .	0.85	0.22
Phosphorus pentoxide . . . . .	—	0.29
Lime, magnesia, ferric oxide (as phosphates) . . . . .	—	0.63
	87.91	12.09

Heidenpriem found in molasses ash:

Potash . . . . .	47.67	51.72 p.c.
Soda . . . . .	8.00	11.43 "
Lime . . . . .	3.12	5.04 "
Magnesia . . . . .	0.10	0.18 "
Carbon dioxide . . . . .	27.94	28.90 "
SO <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub> , Cl, Fe <sub>2</sub> O <sub>3</sub> . . . . .	6.16	3.33 "

*Manufacture of vinasse-cinder (salin, schlempekohle).* The vinasse, a liquid of about sp-gr. 1.028, and always of acid reaction (purposely brought about for the sake of fermentation, *v. supra*), is neutralised with lime, and is then concentrated by evaporation. Since the profitable working of this process depends entirely upon the economical evaporation of a dilute liquid, much ingenuity has been expended on the evaporating apparatus. The heat must act both as top and bottom heat, the flame travelling between two pans, or over the top of a pan covered with an arch, upon which another pan is set so as to be indirectly heated. The most successful and most widely-employed system for this purpose is Porion's furnace, in which the evaporating-surface is largely increased by splashing about the liquid in the fire gases by means of paddle-wheels revolving from 400 to 800 times per minute.

The heat required for evaporating the liquid is produced partly by an ordinary fire, partly by the combustion of the organic substance contained in the vinasse. When the latter has been brought to the syrupy state, say 60°Bé., it is transferred from the iron pan on to the bed of a reverberatory furnace, immediately attached to it, on which it is altogether dried, whereupon it takes fire and itself produces a large amount of heat. This is aided by the nitrates contained in the mass. The heat must, however, be so regulated that the mass is not brought to fusion; when fused it would be *salin*, and it would also contain lower oxidation-products of sulphur. The process is therefore finished when a carbonaceous mass has been formed, a sample of which yields with water on filtration a colourless solution. This is the 'salin brut' or 'vinasse cinder', a product largely sold in this state, and employed chiefly for soft-soap and for the manufacture of saltpetre from Chilean sodium nitrate; it is now generally worked up into potassium carbonate and other salts.

The composition of vinasse cinder varies between *vinasse* according to the soil on which it is grown. Grüneberg (Amtlicher Bericht über die Wiener Ausstellung, 1, 399) gives the following figures as the average composition of this product:

Potassium carbonate . . .	30 to 35 p.c.
Sodium carbonate . . .	18 to 20 "
Potassium chloride . . .	18 to 22 "
Potassium sulphate . . .	6 to 8 "
Insoluble (incl. carbon) . .	28 to 15 "

but the analyses published by Sauerwein, Gohren, Kuhlmann, Esselens, Lefevre, and others, prove that the proportion of the ingredients may vary even more.

A large number of analyses of vinasse cinder are given by Hinz (Fischer's Jahresh. 1893, 389 *et seq.*).

In lieu of burning the syrupy vinasse on the hearth of an open surface, C. Vincent (Compt. rend. 84, 214) runs it, at a strength of 40°Bé., into iron retorts, and carbonises it with condensation of the formed vapours, the recovered liquids being subjected to a special treatment. This extremely ingenious process, by which trimethylamine and methyl chloride were for the first time obtained as commercial products,

together with methyl alcohol and ammonia, was carried out on a large scale at Courrières, in the north of France, but has not extended beyond this. A modification of Vincent's process is that proposed by A. Zwillinger (D. R. P. 38419), who carbonises vinasse, brought to the syrupy state, in a retort by means of superheated steam.

The following description is an outline of Vincent's process. The cinder, obtained by heating the vinasse-residue in closed retorts, is very porous and easy to lixiviate; the potash made from it is very pure, and especially free from sulphate and sulphide. The gaseous products are submitted to a process of condensation quite similar to that usual at gasworks; a little tar and a considerable quantity of aqueous fluid is condensed, and a considerable quantity of gas is left over, which may be used for . . .

The aqueous liquid contains ammonium carbonate, hydrosulphide and cyanide, methyl sulphide, methyl alcohol, . . . and the volatile monobasic fatty . . . neutralised with hydrochloric acid, and the greater proportion of water is removed by distillation. The distillate contains, together with much water, methyl alcohol and methyl cyanide; by re-distilling it with lime, the methyl alcohol can be set free, and calcium acetate remains behind. From 100 kilos. of molasses 1½ litres of methyl alcohol is obtained. The original liquid, concentrated by distillation and allowed to cool, yields a crop of ammonium chloride (about 2 kilos. for 100 kilos. of molasses). The mother-liquor (about 1.8 kilos.) contains principally trimethylamine hydrochloride. It is further concentrated by evaporation, and the dry mass is subjected to . . . At 260° there begins . . . and at 325° the . . .

The gases escaping consist of trimethylamine and methyl chloride, afterwards with much ammonia; they are passed through hydrochloric acid, which retains trimethylamine and ammonia, whilst methyl chloride passes on, is washed with water and collected in a gas-holder. The liquor is concentrated to a boiling-point of 140°C.; on cooling, nearly all the ammonium chloride crystallises out and trimethylamine hydrochloride remains in the mother-liquor. The gaseous methyl chloride is dried, and by means of compression and cooling is condensed to a liquid, boiling at -23°C., which is sent out in strong wrought-iron or copper drums, and used principally in the manufacture of aniline dyes.

The theory of the decomposition of the dry trimethylamine hydrochloride by heat is as follows. At first this salt is, like ammonium chloride, dissociated by heat, and much free trimethylamine is volatilised. The acid residue at a higher temperature undergoes the following reaction:  $\text{N(CH}_3)_3\text{HCl} \rightarrow \text{N(CH}_3)_3 + \text{HCl}$ . This explains the . . . into trimethylamine, methyl chloride, and ammonia.

Elsewhere the recovery of methyl chloride and trimethylamine does not appear to have been attempted, but in several places the ammonia has been recovered by various methods. Thus Baswitz (Dingl. poly. J. 245, 415) runs the vinasse, concentrated to 31° or 41°Bé., in a thin jet into red-hot retorts. The gaseous products pass through a pipe filled with pieces of firebrick and heated outside by waste heat; further on some

tar is condensed, rich in pyrrole and pyridine bases, then the ammonia is absorbed in sulphuric acid; finally the methyl alcohol is condensed by cooling, and the uncondensed gases are returned to the fire. Each retort takes a charge of 360 litres of concentrated vinasse every 12 hours; the produce of 4 retorts is: 87.5 kilos. ammonium sulphate, 30 kilos. liquor containing amines, 4 to 4.5 kilos. methyl alcohol, 57.5 kilos. tar. (The process did not pay when the prices of the above products went down.) H. Hirtzel (Zeitsch. Chem. 11, 346) employs a vacuum apparatus with mechanical stirrer. Borsche and Sohn (Dingl. poly. J. 244, 85) carbonise the vinasse with lime in order to increase the yield of ammonia; they assert that up to 80 p.c. of the nitrogen can be thus obtained as  $\text{NH}_3$ . Similar processes are patented by E. Ernst (*ibid.* 244, 86; 245, 413), by Oppermann, by Gaillett, and by the Waghäusel Sugar Company (*ibid.*). Lederer and Gintl (*ibid.*) carbonise vinasse, or the liquors of the lime and osmose process in revolving drums by a continuous process, the gases being treated for the recovery of ammonia.

Other apparatus for treating vinasse are those of Kux (Dingl. poly. J. 247, 163), of Klauning (*ibid.* 261, 250), of Gontard (*ibid.* 258, 498), and of Theisen (*ibid.* 257, 405).

*Working-up of the vinasse cinder.* The cinder is broken up into pieces of the size of a man's fist, or rather less, and is methodically lixiviated with hot water in the usual way. The liquor is run off at a strength of 23-32°Tw. The black residue (grey after drying) contains from 8-12 p.c. of alkaline salts (partly being potassium sulphate, partly not soluble in water), 20-40 p.c. carbonaceous matter, containing a little nitrogen, 15-30 p.c. calcium carbonate, and a few p.c. of other earthy matters. The first evaporation takes place by means of steam coils, and is carried to 74-82°Tw., the concentration being higher in summer than in winter. Most of the potassium sulphate is now precipitated as a fine mud; after two hours' settling the clear liquor is allowed to cool down, when impure potassium chloride crystallises out. According to whether the salts are at once subjected to methodical washing or not, they contain less or more potassium carbonate, as shown by the analyses of Tissandier (Wagner Jahr, 1868, 286). The analysis of a large number of French samples of such chloride (by Blattner, unpublished) yielded—

Potassium chloride	66.21 to 87.55 p.c.
Potassium sulphate	5.27 " 19.86 "
Potassium carbonate	0.10 " 6.49 "
Sodium carbonate	0.40 " 4.57 "
Water	1.40 " 8.79 "

This product is principally employed for conversion into sulphate, and then into carbonate, by the Leblanc process.

The mother-liquor is further evaporated by open fire in wrought-iron pans with flat or saddle-shaped bottoms, in three stages, down to 127°-142°Tw. During evaporation, monohydrated sodium carbonate is separated, which must be fished out, and is purified by washing and calcining; on cooling down, to 97°Tw., principally potassium chloride crystallises out. This is washed like that obtained previously,

but beyond that strength the crystals consist principally of a potassium-sodium carbonate  $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ , together with some hydrated potassium carbonate,  $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ . The double carbonate is re-dissolved in a little hot water and evaporated down to 127°Tw., during which operation nearly all the sodium carbonate separates as  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , and is removed by fishing. The mother-liquor from this operation is boiled down, together with the mother-liquor formerly obtained, and is, after proper settling, calcined in a reverberatory furnace. It yields a crude potassium carbonate containing:

$\text{K}_2\text{CO}_3$	80-84 p.c.
$\text{Na}_2\text{CO}_3$	3-10 "
KCl	3-4 "
$\text{K}_2\text{SO}_4$	3-4 "
$\text{K}_2\text{SiO}_3$	0.25-0.5 "
$\text{K}_2\text{HPO}_4$	0.3-1.5 "
Insoluble	0.1-0.2 "

Bauer (D. R. P. 191105) obtains technically pure potassium carbonate from vinasse cinders by heating the solution to 53°Bé., separating the precipitated salts, heating the purified solution to 90°, until a concentration of 56°-62°Bé. is attained and allowing to cool, whereupon potassium sodium carbonate crystallises out and is decomposed into  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  by fusing and keeping at 50°.

Part of the potassium sulphate is formed from thiocyanate; and this salt itself is partly formed during the evaporation from potassium ferrocyanide and sulphide as witnessed by the ferrous sulphide, always precipitated together with the fished out soda. This purification from iron is very important, and is sometimes promoted by purposely adding potassium sulphide to the liquors in sufficient quantity to precipitate the iron. Otherwise, even white potash is discoloured on contact with the air. Once calcined potash, when treated as above, is sufficiently pure and white, but otherwise it can be purified by re-dissolving, settling, and recalcining. The analyses given at top of next page show the position of different descriptions of vinasse potashes.

6. *Potash from suint.* The 'suint' or 'yolk,' which forms a third or more of the weight of raw sheeps' wool, was proved by Chevreul to contain, together with many other substances, a considerable quantity of potash, combined with fatty acids to form a soluble soap. Maumené and Rogelet were the first, in 1859, to utilise this for recovering potassium carbonate from the suint. The example has been followed elsewhere, but not to any great extent. 100 parts of raw wool are stated by Maumené to yield from 14 to 18 parts of salts, or about 5 parts of potassium carbonate; hence the 60,000 tons of wool annually imported into the United Kingdom ought alone to yield about 3000 tons of potassium carbonate, none of which is recovered up to the present. Even at Roubaix, Rheims, and Elbeuf, in lieu of the 1200 tons obtainable from the wool consumed there, only 150 tons per annum are actually recovered; the rest of suint potashes in France, many probably does not exceed 2000 tons per annum. This is all the more to be regretted as the potash contained in suint in the ordinary course of washing raw wool in a



## ANALYSES OF COMMERCIAL VINASSE POTASHES.

Origin	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> SO <sub>4</sub>	KCl	Insol.	H <sub>2</sub> O	Analyst
French potash . . .	53.9	23.1	2.9	19.6	—	—	Pesier
Valenciennes potash . . .	79.0	14.3	3.9	2.8	—	—	Grüneberg
Refined potash . . .	92.68	3.98	0.43	2.45	0.06	0.50	Tatlock
" " . . .	91.22	2.86	2.76	1.92	0.08	0.85	"
" " . . .	90.83	2.68	2.67	2.52	0.27	0.90	"
" " . . .	90.25	2.52	3.81	2.92	0.21	0.45	"
Belgium crude ash . . .	43.0	17.0	4.7	18.0	—	—	Grüneberg
" " . . .	34.3	13.0	11.0	23.5	—	—	"
Magdeburg crude ash . . .	32.9	18.5	14.0	16.0	—	—	"
" " . . .	27.1	18.0	10.0	9.5	—	—	"
Wäghäusel (refined) . . .	94.39	trace	0.28	2.41	0.18	—	v. Groningen
" " . . .	88.73	6.45	2.27	1.01	—	—	Keller
" " . . .	78.10	13.33	2.31	3.21	3.05	—	Tissandier
" " . . .	81.22	13.15	1.78	3.25	0.80	—	"
" " . . .	91.25	4.73	0.80	2.61	0.61	—	"

running stream does not return to the soil, but merely contributes to the pollution of water-courses. But the difficulty in the way of the general adoption of the recovery process is, that it does not pay on the small scale, and that neither producers nor consumers of wool, in the majority of cases, will relegate the scouring of their wool to a central manufactory, where it is doubtful whether the different parcels can be kept entirely distinct. It is thus preferred by . . . to wash their own wool, and, if . . .

the . . . upon their meadows. . . working the wool for suint . . . Instead of washing the . . . running stream, and afterwards scouring it with soap, soda, or putrefied urine, the wool is, before . . . process, submitted to a . . . with cold water, either in a series of casks or tanks, or in mechanically-acting washers, for instance that constructed by H. Fischer (Dingl. poly. J. 218, 484; 229, 446). The dilute washings are always utilised for the first treatment of a fresh quantity of wool. Thus a brown liquor of about sp.gr. 1.12 is obtained, which is evapor-

ated in iron pans of very different constructions where the fuel can be efficiently utilised—for instance, in the reverberatory furnace of Werotte, in which the flame is drawn through the liquid itself by means of an exhaustor; or by means of discs fixed on a shaft revolving in the boiling-down pan. Thus a pasty mass is obtained, which is either calcined in an open furnace or submitted to destructive distillation in gas retorts, in order to recover ammonia and illuminating gas. The carbonaceous residue is lixiviated and the liquor is treated similarly to that obtained from vinasse cinder, producing, by fractional evaporation and crystallisation, successive crops of potassium sulphate and chloride. But as suint contains but little soda (in the case of inland-fed sheep only 2.3 Na<sub>2</sub>O to 100 K<sub>2</sub>O, with sheep fed on the sea coast 13 Na<sub>2</sub>O to 100 K<sub>2</sub>O), the crystallisation of the double carbonate of potassium and sodium does not take place, the liquor being directly brought to dryness and calcined.

Suint potash, if unadulterated, in fact contains but little soda, as can be seen from the following analyses:—

					From Verviers					First quality		Second quality
					Tissandier			Werotte		Tatlock		
K <sub>2</sub> CO <sub>3</sub> . . . . .					71.52	79.01	72.25	68.50	64.30	91.20	89.41	80.57
Na <sub>2</sub> CO <sub>3</sub> . . . . .					4.96	5.15	5.14	3.20	3.10	4.39	3.83	2.48
K <sub>2</sub> SO <sub>4</sub> . . . . .					2.48	3.03	3.33	2.10	2.49	0.52	0.17	4.75
KCl . . . . .					5.88	6.12	7.04	12.50	16.88	1.97	1.67	4.51
K <sub>2</sub> SiO <sub>3</sub> . . . . .					—	—	—	8.50	8.00	—	—	—
Insoluble . . . . .					11.98	5.28	11.19	1.48	1.55	0.04	0.06	0.30
Water . . . . .					2.83	1.20	1.05	2.77	2.80	1.60	4.70	7.25

The following analyses, by W. Graff, give the . . . potash, made in Germany—viz. (a) by the simple steeping process, (b) and (c) by methodical lixiviation:—

	a	b	c
K <sub>2</sub> CO <sub>3</sub> . . . . .	31.16	75.01	71.40
K <sub>2</sub> SiO <sub>3</sub> . . . . .	17.44	0.62	1.50
K <sub>2</sub> HPO <sub>4</sub> . . . . .	0.50	0.71	—
K <sub>2</sub> SO <sub>4</sub> . . . . .	2.00	4.12	5.32
KCl . . . . .	3.93	5.68	6.74
Na <sub>2</sub> CO <sub>3</sub> . . . . .	3.15	3.07	4.65
H <sub>2</sub> O . . . . .	1.22	1.30	4.72
Insoluble . . . . .	40.60	9.49	5.77

**Potassium hydroxide (Caustic potash).** The majority of soap-makers prefer causticising their own potassium carbonate, as they mostly do not require to do this thoroughly. Still the manufacture of caustic potash in the solid state is carried on to some extent on the large scale, with black-ash made by the Leblanc process from potassium sulphate, precisely in the same manner as caustic soda is made, so that we can refer to that article. In this place we need only give the analyses (by Tatlock) of some

samples of caustic potash made on the large scale:—

	White	Brown or cream	
Potassium hydroxide . . . . .	77.64	75.64	74.05
Potassium carbonate . . . . .	4.62	2.54	3.14
Potassium sulphate . . . . .	0.38	0.21	0.69
Potassium chloride . . . . .	2.29	0.93	2.26
Potassium nitrite . . . . .	0.87	—	—
Sodium hydroxide . . . . .	4.67	2.59	3.20
Soluble silica and alumina . . . . .	0.30	0.20	0.55
Insoluble matter . . . . .	0.02	0.22	0.69
Water . . . . .	8.84	17.80	15.80
Available potash, $K_2O$ . . . . .	68.33	65.24	64.31
Available alkali, calculated as $K_2O$ . . . . .	73.83	68.28	68.08

Graff (D. R. P. 88003) prepares potassium hydroxide from vinasse cinder. The solution of this product is causticised, concentrated by evaporation, separated from the potassium sulphate and chloride crystallising out and now contains only sodium and potassium hydroxides. The necessary quantity of potassium carbonate is added to convert the sodium present into the double salt  $KNaCO_3$ , which is removed by concentration and cooling, leaving pure KOH in solution. Or else the potassium hydroxide is separated from the potassium-sodium carbonate by evaporating the mixture to dryness and extracting the KOH by means of alcohol.

N. T. Bacon (D. R. P. 99344) employs a hot, concentrated solution of strontia into which solid potassium carbonate is introduced. The conversion into KOH and  $SrCO_3$  is almost instantaneous.

The Chemische Fabrik Griesheim (D. R. P. 108500) gives detailed prescriptions for the purification of caustic potash solution by diffusion. The Salzbergwerk Neustassfurt

(D. R. P. 117748) effect such a purification by fractionated crystallisation at  $60^\circ$ .

I. A. Reich (D. R. P. 161795) prepares caustic potash by boiling potassium silico-fluoride with caustic lime.

Crystallised potassium silicate is obtained by Salzbergwerk (D. R. P. 189835) by conducting the concentration of the solution in a special manner.

**Potassium silicate.** Potassium silicate, or soluble potash glass, has approximately the formula  $K_2O, 4SiO_2$ . It is prepared exactly like the more common soluble soda glass, by fluxing together white potassium carbonate in a reverberatory furnace with a little charcoal, which aids in expelling the carbon monoxide. The following is stated by N. Fuchs to be 100 parts of sand and 45 parts, commercial good charcoal 3 parts, to be fused for 5 or 6 hours until no more gas escapes; the product is 58 parts of silicate. O. Schür prescribes: 90 sand, 62.5 potashes, 1.5 charcoal; product 112.5 to 115 soluble glass. Some manufacturers employ potassium sulphate in lieu of carbonate, together with a larger proportion of charcoal, but this is much more difficult than with potassium silicate. Potassium silicate is a transparent glass, tinged a bluish green, which is either sold as such, or in the state of a thick solution, prepared by boiling it with water for a long time, preferably under pressure. Frequently a mixed silicate of soda and potash is produced, either by using a mixture of potash and soda in the fluxing process, or by mixing the solutions.

Potassium silicate can be obtained also by dissolving very finely-divided silica (in the shape of ignited and ground flints, or of kieselguhr, or Farnham stone) in a very strong solution of caustic potash, by prolonged boiling, or in a shorter time by boiling under pressure. This process is actually used for the manufacture of sodium silicate.

Analyses, by Tatlock, show the composition of commercial potassium silicate:—

	Solid			Liquid	
	a	b	c	d	e
Potash (as silicate) . . . . .	23.54	22.91	9.46	4.31	3.49
Soda (ditto) . . . . .	1.28	1.28	1.52	4.20	1.80
Silica . . . . .	65.60	66.84	23.28	24.32	16.64
Potassium sulphate . . . . .	0.87	1.08	0.67	0.61	1.48
Potassium chloride . . . . .	0.48	0.48	0.41	0.67	3.52
Alumina and ferric oxide . . . . .	0.40	0.32	—	—	—
Water . . . . .	7.83	7.09	64.66	65.89	73.07

The total quantity of potassium silicate manufactured is small, compared with that of sodium silicate. It is used in soap it can be nearly equal to soda ash per sodium silicate, and for a few other purposes.

**Potassium nitrate** (*Saltpetre, nitre*). Potassium nitrate  $KNO_3$  is first mentioned by Geber, in the eighth century, and again by the alchemists of the thirteenth century. Agricola in

1546 gives a description of its manufacture from saltpetre earth, which does not materially differ from the present process. The artificial preparation of this substance from Chilean sodium nitrate is comparatively a recent process, due in the first instance to the greatly-increased demand produced by the Crimean war, but this manufacture has gained very large dimensions, and is now much more important than the working of natural saltpetre earths.

## POTASSIUM.

*Manufacture of saltpetre from natural earths.* Such earths are found principally in East India, where the district of Bengal, in Bengal, is the most important one in respect, and whence nearly all the saltpetre still manufactured is derived. Other deposits are found in Egypt, Persia, Italy, Apulia, Kentucky, &c., none of which is of more than local importance.

The raw material occurs only occasionally in strata or nests; it is mostly a product, usually re-formed by the action of atmospheric air upon nitrogenous organic matter in the presence of bases, such as lime, magnesia, and potash (for which, in Peru, near the coast, soda is substituted). The organic matter is not simply oxidised by atmospheric oxygen; the process of 'nitrication' takes place except in the presence of certain microbes, as first proved by Schläsing and Mintz (Compt. rend. 84, 602; 85, 1018; 86, 102), and confirmed by many subsequent experiments.

Whether the formation of ammonia is an inseparable intermediate link remains an open question. The nitrification process is, of course, more intense in hot countries, where it is assisted by the abundance of organic matter, and by the moist and warm atmosphere. It is dependent upon a supply of nitrogenous substances, and has nothing to do with the direct formation of nitric acid from atmospheric oxygen and nitrogen by the electric discharge. Saltpetre earth is, consequently, found in the neighbourhood of villages, towns, urine, &c., yields an abundant supply of organic nitrogen. In Bengal it is collected in a special caste, the 'Sorawallahs,' partly from the soil, partly from the surface of mud-brick cottages, &c., by scraping off the uppermost layers which show a white efflorescence.

The following analyses show the composition of some Indian saltpetre earths:—

—	Tirhāt (Steven- son)	Tirhāt (J. Davy)	Ceylon (J. Davy)
Potassium nitrate .	0.7	8.3	2.4
Calcium nitrate .	0.9	3.7	—
Magnesium nitrate .	—	—	0.7
Sodium chloride .	2.7	—	—
Calcium sulphate .	1.4	0.2	—
Magnesium sulphate .	—	0.8	—
Calcium carbonate .	—	—	0.2
Insoluble in acids .	44.3	35.0	26.5
Water and organic substances .	50.0	40.0	60.8
	—	12.0	9.4

Ganges mud, according to Warnford Lock, contains 8.3 p.c. potassium nitrate, and 3.7 p.c. calcium nitrate. This earth is lixiviated in earthenware dishes, or wooden boxes, or in pits dug in the ground and made tight by a clay puddle. The liquor is concentrated in iron pots, or sometimes only by solar heat, and a crop of very crude saltpetre is thus obtained. The mother-liquor is further evaporated to obtain common salt, and the last mother-liquor, which contains a large quantity of calcium and magnesium nitrate, is mostly run to waste. Occasionally a somewhat more rational process is pursued, by mixing wood-ashes with the saltpetre earth previous to lixiviation, or adding such ash to the solution during concentration; the potassium carbonate of the wood-ash then converts the earthy nitrates into potassium nitrate. The crude saltpetre, obtained from the clarified liquor by slow evaporation in earthenware pots, is called 'dhouah'; it contains from 45 to 70 p.c.  $\text{KNO}_3$ , and is re-crystallised by native merchants, who sell it in this state as 'kalmee.' The following analyses, by Tatlock, show the composition of some samples of Indian saltpetre:—

—	Bengal ordinary 1	Commercial 2	Bombay 1	Crude 2
Potassium nitrate . . . .	51	89.36	72.46	36.06
Potassium sulphate . . . .	0.89	0.75	0.13	2.64
Potassium chloride . . . .	0.84	4.57	6.65	—
Sodium nitrate . . . . .	—	—	—	0.26
Sodium chloride . . . . .	0.20	0.31	17.41	47.43
Sodium sulphate . . . . .	—	—	0.19	2.21
Magnesium nitrate . . . . .	—	1.97	0.17	2.08
Insoluble . . . . .	0.21	0.14	0.14	1.55
Water . . . . .	1.35	2.90	2.85	7.95

A sample of the 'refuse salt' left behind on salting the first crop of crude saltpetre, and containing 8.83  $\text{K}_2\text{SO}_4$ , 13.15  $\text{KNO}_3$ , 21.14

According to Ljubawin (Fischer's Jahresh. 1862), there is a large deposit of saltpetre in the Khanat of Khiva, south-west of Bukhara, of the following composition:—

Insoluble in water . . . . .	27.89 p.c.
Insoluble in hydrochloric acid . . . .	17.14 "
Carbon dioxide . . . . .	5.73 "
Insoluble in acids . . . . .	48.42 "
	99.18 "

The portion soluble in water contains:—

$\text{KNO}_3$ . . . . .	5.52 p.c.	$\text{CaSO}_4$ . . . . .	3.25 p.c.
$\text{NaNO}_3$ . . . . .	4.05 "	$\text{MgSO}_4$ . . . . .	0.66 "
$\text{Mg(NO}_3)_2$ . . . . .	1.04 "	Total nitrates	10.61 "
$\text{NaCl}$ . . . . .	12.90 "		

Saltpetre earths are found, and are worked by processes quite similar to those used in India, in some places in Persia, Egypt, Spain, Hungary (near Debreczin) and elsewhere.

An artificial saltpetre earth is, or formerly was, prepared in some European countries (Hungary, Switzerland, Sweden) by mixing a porous soil containing much calcium carbonate, with decaying animal substances; for instance,

by preparing such a soil underneath the floor of stables where cattle and sheep are kept, the urine penetrates into the soil, and there undergoes the nitrification process. In Sweden, where formerly every landowner was obliged to furnish to Government a certain quantity of home-made saltpetre, all sorts of artificial nitrates were made up in this manner, in special 'saltpetre plantations.' About 100 tons per annum were made in Sweden in this way, but this process has been given up as unprofitable. In France, during the wars of the Revolution, when Indian saltpetre was inaccessible, that process was made compulsory by a decree of the Convention, and it is asserted that 2000 tons per annum were then made in this way; but there also the home manufacture had to be given up as soon as saltpetre could be imported from the East. Since the manufacture of saltpetre from nitrate of soda is making a severe competition with the Indian saltpetre, it seems that the French look to European sources for their supply; here the nitrogenous substances are better utilised for agricultural purposes.

Another kind of crude saltpetre, made from the urine of man, is the working of 'caliche' for saltpetre. Sometimes sent to Europe from South America. It contains from 16 to 26 p.c. of potassium nitrate, 51 to 77 p.c. of sodium nitrate, 1 to 3 p.c. of calcium chloride, and 1 to 3 p.c. of sulphates and iodates. Its value is hardly greater than that of its equivalent of ordinary commercial sodium nitrate.

According to Sacc (Compt. rend. 90, 84), in Bolivia, near the village of Arané, East of Cochabamba, a large deposit has been found of the following average composition: 60.7 potassium nitrate, 30.7 borax, traces of common salt, and water, 8.6 organic matter. If this were confirmed, it would be very valuable indeed.

*Refining of saltpetre.* The East Indian saltpetre, before it can be used for the manufacture of gunpowder and other purposes, must be purified, especially from chlorides. This is done on a very large scale in England, France, and Germany (especially at Hamburg). The most usual is the French method. In an iron or copper pan 1050 kilos. saltpetre is dissolved in 600 litres of water at a gentle heat; the solution is brought to boiling heat, and another 1800 kilos. of saltpetre is dissolved in it. When employing these proportions with saltpetre containing about 20 p.c. of chlorides, the nitrate is dissolved completely, the chlorides but partially. The latter are fished out with a perforated ladle. If calcium or magnesium salts are present, potassium carbonate is added until a fairly alkaline reaction has been produced. The hot clear liquor is diluted with 300 litres of water, a solution of 1 kilo. glue in 20 litres of hot water is stirred into it, and the whole brought to boiling again. The glue combines with the organic substances present forming a scum, which rises to the surface and is carefully removed. When no more scum rises to the surface, the liquor is allowed to settle for 24 hours, and then cooling down below 90°C., and

cools. As soon as the liquor is constantly clear, the liquid is constantly stirred, or better by machinery. Thus the potassium nitrate separates as minute, floury, crystals,

which do not, like large crystals, inclose mother-liquor in hollow spaces. The crystal flour is drained; the mother-liquor (500 to 600 kilos.) is used over again in dissolving fresh saltpetre.

The small crystals must now be washed to remove all adhering mother-liquor. This is done in vessels provided with a false bottom, covered with linen. When all liquor has drained off, the bottom tap is closed, cold water is sprinkled upon the salt by means of a rose, the whole is allowed to stand for some hours, and only then the liquor is run off. This is repeated several times, until the liquor shows next to no reaction for chloride. The last liquors are used in a new operation for the first washings. In this way the chlorides may be brought down to 0.005 p.c.

The drained crystal flour is dried in stoves or frames covered with canvas, or better on steam-heated pans, with mechanical stirring (just as they have been described for potassium chloride), and is mostly sold in this shape. Sometimes it is required in the shape of large crystals, which are very easily obtained by dissolving the flour in a small quantity of hot water and allowing the liquor to cool quietly and slowly. Exceptionally, it is fused into cakes or drops, which always contain a little nitrite (the 'sal prunellæ' or 'nitrum tabulatum' of the old chemists).

*Artificial potassium nitrate from nitrate sodium.* 'Artificial saltpetre' was first made on a small scale by Longchamps and Anthon, with the aid of Chilean sodium nitrate and of potassium chloride, which, however, at that time was only obtainable from kelp, and was too expensive. When, in consequence of the increased demand for saltpetre during the Crimean war, especially in Russia, the manufacture of that substance from Chilean sodium nitrate became more remunerative, it was first carried out, in 1853, by Nöllner, Grineberg, and others, with the aid of caustic potash and of Russian potassium carbonate; later on, more cheaply, with that of *vinasse cinder* ('schlempekohle,' cf. p. 359), which was used directly, without any separation of the salts. For this purpose sodium nitrate and a corresponding quantity of vinasse cinder were mixed, and then by the reaction  $\text{NaNO}_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{KNO}_3 + \text{Na}_2\text{CO}_3$  anhydrous potassium carbonate was produced, which was fished out of the boiling liquid, together with the sodium carbonate originally present, and with the less soluble potassium salts, while the potassium nitrate remained dissolved at boiling heat and only crystallised out on cooling. The mother-liquor yields a mixture of about 53 parts NaCl, 31  $\text{Na}_2\text{CO}_3$ , and 10  $\text{K}_2\text{SO}_4$ , which is used by soap-makers (cf. Dingl. poly. J. 118, 200; 155, 418; 163, 314; 166, 75; Chem. Zentr. 1872, 491). This process has been given up long ago, principally because the separation of the salts is too difficult and the value of potassium carbonate is too great.

The separation of the substances is easier when *caustic potash* is employed, in which case the reaction produces potassium nitrate and caustic soda; the mixture can then be allowed to cool. The potassium nitrate is all but completely separated as fine crystals, and sodium hydroxide, with some impurities, remains in

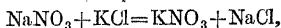
solution. By further concentrating this, solid caustic soda can be obtained. This process was carried out by Nöllner, Landmann, and Schnitzer (Dingl. poly. J. 117, 68; 162, 182) by adding lime to the boiling mixture of potassium carbonate and sodium nitrate until the alkali was causticised, whereupon the liquid was separated from the lime-mud, concentrated by evaporation, and allowed to crystallise. Much more rational than this was the process carried out at St. Helens in 1864 (*ibid.* 182, 385), decomposing potassium chloride by sulphuric acid, converting the potassium sulphate by Leblanc's process into a kind of black-ash, dissolving and causticising the caustic solution to sp.gr. 1.50, adding an equivalent quantity of sodium nitrate and allowing the potassium nitrate to crystallise by cooling. The mother-liquor was further concentrated, during which operation some salts were separated and fished out, and on cooling yielded a second crop of potassium nitrate; the second mother-liquor was worked up as caustic soda. This process does not seem to be worked now.

The process of Bolley (Wagner's J. 1860, 201; 1866. 227), converting sodium nitrate by means of barium chloride into barium nitrate, and converting this by potassium sulphate into barium sulphate ('permanent white') and potassium sulphate, is evidently not fit for general use, and can only pay in very exceptional circumstances.

The only process now in practical use is that of employing *potassium chloride*, originally proposed by Longchamps, and worked out by Anthon (since 1840, but more especially in 1858, Dingl. poly. J. 149, 39) in the shape in which it is now carried out. A theoretical study of the conditions of equilibrium between the reciprocal pairs of salts: KCl, NaNO<sub>3</sub> and NaCl, KNO<sub>3</sub>, has been made by Meyerhoffer (Ber. 1904, 261, *et seq.*). The technical forms of the process have been described by Lunge (Dingl. poly. J. 182, 385) and Pick (*ibid.* 215, 222), and it is carried out in several modifications, the best of which will now be described.

Stassfurt 'muriate of potash,' containing not less than 80 p.c. KCl, and commercial sodium nitrate (95 p.c.), are brought together with mother-liquors from a previous operation and with the liquid obtained by washing the nitre bags. (The washed nitre bags, when dry, are exceedingly easily inflammable, and must be treated with the necessary caution.) The operation is performed in covered wrought-iron cylinders, 8 ft. diameter and 6½ ft. high, provided with a mechanical stirrer, a steam coil, and a tap for an open jet of steam; also with a 6-inch pipe in the cover, through which the steam given off in the cylinder is passed under the double bottom of the mother-liquor tank. The liquor is first concentrated by means of the steam coil to sp.gr. 1.53, adding a little oil in case of frothing, whereupon the materials are charged through the man-hole, first 3 or 3½ tons of sodium nitrate, then the corresponding quantity of potassium chloride, which is so calculated that a very slight excess of nitrate is present. The whole is boiled for half-an-hour to complete the decomposition, and is then run through a 4-inch tap on to the filter or strainer, consisting of a tank 8 by 8 by 5 feet, with a canvas-covered

false bottom at a height of 4 ins. above the true bottom, and a steam-pipe between the two for heating. Here the sodium chloride



which, owing to its relatively slight solubility in the hot concentrated solution, has been almost entirely precipitated in the solid form, is retained on the filter, while a liquor of sp.gr. 1.63 and a temperature of 95°C. runs off into the coolers. The common salt left on the filter is covered with hot mother-liquor, which is run off at a strength of 1.50 to 1.53, also into the coolers. The washing is then continued with liquors of decreasing strength, ultimately with pure water, until the salt contains only 0.6 to 0.9 p.c. of nitrate; at some works they go down to 0.25 p.c. The coolers are shallow iron vessels provided with either oscillating or revolving agitators, which can be lifted out of the liquid. The liquor is kept in agitation during the whole time of cooling, which, with a depth of 8 ins. in the vessels, ought to be finished in 30 to 36 hours. Sometimes this is hastened by a stream of water circulating on the outside of the vessel.

The mother-liquor, of sp.gr. 1.345-1.357, is run off into tanks provided with a double bottom, where it is heated by waste steam in order to be used over again at the first operation. Such mother-liquors are composed as follows. 100 parts by volume contain:

	<i>a</i>	<i>b</i>	<i>c</i>
Potassium nitrate	29.40	25.5	26.4
Sodium chloride	25.72	14.2	17.18
Sodium sulphate	1.32	1.06	1.81
Magnesium chloride	2.10	6.2	8.19
Sodium nitrate	—	10.6	7.19
Sodium iodide	—	—	0.76

(*a*, sp.gr. 1.348 at 19°; *b*, sp.gr. 1.395 at 17.5°; *c*, remaining after working up 5000 tons of Chilean nitre).

The crude saltpetre flour, containing 7-9 p.c. NaCl, and 0.5-0.7 p.c. MgCl<sub>2</sub>, is drained on one side of the cooler, and is washed with the liquor resulting from the refined saltpetre, with the same liquor, until the chloride has come down to 0.8-2 p.c. It is then refined by dissolving it in washings of the pure salt to sp.gr. 1.53-1.55, filtering as above, and running it into iron coolers; in doing this, a very small quantity of ultramarine is added, to neutralise the discolouration produced by a small quantity of iron. Here a mother-liquor of the following composition is produced:

	<i>a</i>	<i>b</i>
Potassium nitrate	20.91	23.4
Sodium nitrate	1.02	—
Sodium chloride	5.94	4.4
Sodium sulphate	0.12	—
Magnesium chloride	0.78	1.1

(*a*, sp.gr. 1.184 at 17°; *b*, sp.gr. 1.180 at 18.5°).

The crystals produced at the same time still contain 0.25 to 0.75 p.c. NaCl, and must be purified by washing them with water in copper-lined iron vessels, in the manner described above for potassium chloride; this produces a liquor of sp.gr. 1.075-1.083. The washed salt is drained, and is dried upon shallow, circular cast-iron pans, heated by means of internal steam channels; a revolving shaft moves the

salt about by means of scrapers forced down by springs, and a conical roller at the same time crushes any lumps formed in drying. Each pan dries nearly 4 tons of nitrate in 24 hours. Unavoidably, some crusts are formed at the bottom, which must be knocked off once a day. The dried saltpetre need only be passed through a sieve to be ready for packing into casks.

It is asserted that, when German muriate of potash is mixed with magnesium chloride may render it deliquescent; this is to be counteracted by adding as much soda-ash as will throw down the magnesia. Muriate of potash made from kelp contains no magnesium chloride, but from 6 to 8 p.c. of sulphate, which does not decompose with nitrate as easily as the chloride. In Germany the above-mentioned drawback has never been found; nor can it be conceived that a mode of manufacture which actually brings down the total chloride to 0.01 p.c. should leave anything whatever of the extremely soluble magnesium chloride in the saltpetre.

The 'saltpetre salt'—that is, the impure sodium chloride formed in this manufacture—contains about 98 p.c. of NaCl in the dry state, with 0.25 to 0.9 KNO<sub>3</sub> and slight quantities of other matters. The nitrate makes it unfit for decomposing with sulphuric acid on account of the strong action on the iron pans; it is used for agricultural purposes, and for roasting the cinders from cupreous pyrites in the process of copper-extracting by the wet method.

**Potassium arsenate** KH<sub>2</sub>AsO<sub>4</sub> (Macquer's salt) is manufactured by fusing together equal parts of potassium nitrate and white arsenic (arsenious oxide), dissolving the mass in water, and evaporating; on cooling the liquor the arsenate crystallises out in large, soluble, quadrate crystals, which do not deliquesce in the air. This salt is used in calico-printing as a substitute for cow-dung.

**Potassium dichromate** *v. art.* CHROMIUM.

**Potassium cyanides, ferrocyanide and ferricyanide, cf. CYANIDES.**

**Potassium phosphate.** The Stassfurter Chemische Fabri. and Grüneberg (D. R. P. 84954) decompose calcium phosphate with sodium sulphate, remove the precipitated gypsum, add to the solution of sodium phosphate the theoretically required quantity of potassium sulphate and cool down to +4°; Glauber's salt crystallises out and the solution contains primary potassium phosphate KH<sub>2</sub>PO<sub>4</sub>.

G. L.

**POTATO, *Solanum tuberosum* (Linn.).** This plant, a native of America, is grown for the sake of its underground tubers or thickened stems. These contain large stores of starch and other formative materials intended as nourishment for future plants. Each tuber has several 'eyes' which are compound buds, capable of producing one or more stalks. Many varieties are known, differing in colour, size, shape, and composition.

The following figures illustrate the variation in composition which has been observed:—

Water	Protein	Fat	Soluble carbo-hydrates	Crude fibre	Ash
68-82	0.5-3.5	0.05-0.80	12-26.5	0.3-1.4	0.4-1.5

The average composition (König) may be taken as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
75.8	1.8	0.2	20.5	0.7	1.0

Of the total nitrogen, about half exists in non-proteid form, chiefly as leucine, xanthine, and tyrosine. The tyrosine of the potato consist of soluble in dilute salt solution and showing coagulation on heating, incipient at about 60°, but not complete until 80°, and a proteose (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 575). The characteristic poisonous constituent of potatoes is *solanine* C<sub>52</sub>H<sub>93</sub>NO<sub>13</sub>, a crystalline substance melting at 244° and almost insoluble in ether and alcohol. It is decomposed by dilute HCl, yielding *solanidine* C<sub>40</sub>H<sub>61</sub>NO<sub>2</sub> (m.p. 191°), soluble in hot alcohol, and a sugar (Firbas, Monatsh. 1889, 10, 541). An amorphous substance—*solanine* C<sub>52</sub>H<sub>93</sub>NO<sub>13</sub>—which also yields solanidine when heated with hydrochloric acid, and which is apparently the anhydride of solanine—is also present in the shoots of the potato.

The sugars formed by the hydrolysis of solanine are dextrose and rhamnose, according to Zeisel and Wittmann (Ber. 1903, 36, 3554), whilst Votoček and Vondraček (*ibid.* 1903, 36, 4372) showed that maltose is also produced. This was also observed by (Monatsh. 1905, 26, 4). The formation of a dextro-rotatory sugar which he thought was probably a polysaccharide.

According to Wintgen (Zeitsch. Nahr. Genussm. 1906, 12, 113), the amount of solanine in potatoes is very small, the highest and lowest amounts found being 0.1059 and 0.0172 parts per thousand. No increase in the amount was observed after prolonged storage, even in potatoes when the shoots were present. He concludes that the amount of solanine is so small that no poisonous effect need be feared.

Nevertheless care should be taken that animals do not eat the young shoots of sprouted potatoes, for they have been found to contain as much as 50 parts of solanine per thousand. Potatoes, greened by the action of light, also may contain as much as 3 times the normal proportion of solanine (Kellner). According to Weil (Arch. Hygiene, 1900, 38, 330), certain bacteria induce the formation of solanine in potatoes. Some samples of potatoes contained 0.38 p.c. of solanine.

Of the nitrogen-free extract, starch constitutes the greatest portion, but sugar (varying from about 0.5 to 1.2 p.c.) and pentosans are also present. The starch occurs in large grains—the largest from 75μ to 110μ in length—of an oval, ovate, ellipsoidal or conchoidal outline, possessing a distinct hilum, generally situated in the narrow end of the grain and with well-marked, concentric striations. Potatoes also contain small quantities of free acids, among which citric, succinic, and oxalic acids are probably the chief.

For many purposes, the commercial value of potatoes depends upon their content of starch, and it is found that this may be deduced with sufficient accuracy (to about 1 p.c.) from a determination of the specific gravity of the

tubers. This can be done by means of specially designed balances, capable of weighing about 5 kilos. of potatoes in air and in water. According to tables calculated by Behrend, Marcker, and Morgen, the correlation between specific gravity of the tubers, proportion of total dry substance, and starch content, is as follows:—

Specific gravity	Percentage of dry matter	Percentage of starch
1.080	19.7	13.9
1.085	20.7	14.9
1.090	21.8	16.0
1.095	22.9	17.1
1.100	24.0	18.2
1.105	25.0	19.2
1.110	26.1	20.3
1.115	27.2	21.4
1.120	28.3	22.5
1.125	29.3	23.5
1.130	30.4	24.6
1.135	31.5	25.7
1.140	32.5	26.7
1.145	33.6	27.8
1.150	34.7	28.9

Obviously such a table can only claim approximate accuracy since the proportion of starch to other solid matter is variable in different tubers.

Balland (Compt. rend. 1897, 125, 429) found, as the result of the examination of a large number of varieties of potatoes grown in France, the following:—

	Weight of tuber	N-com- grms. Water	pounds	Fat	Starch and sugar	Fibre	Ash
Maximum	420.0	80.0	2.8	0.14	29.9	0.7	1.2
Minimum	23.0	66.1	1.4	0.04	15.6	0.4	0.4

The ash generally contains traces of manganese. The acidity varied from 0.07 to 0.25 p.c.

Forfang (Bied. Zentr. 1904, 33, 392) found, as the average of ten analyses of potatoes grown in West Norway—

Water 75.6 p.c., total dry matter 24.4, starch 15.2, sugar 2.2, crude fibre 0.7, furfuroids 0.7, total N 0.4, fat 0.04, and ash 1.0 p.c.

Coudon and Bussard (Compt. rend. 1897, 125, 43) have examined the separate portions of potatoes. They find that after the removal of the skin, there are three distinct layers, differing in composition—the cortical layer containing the highest proportion of starch and the lowest proportion of water and the external medullary layer

composition and the internal medullary layer which is richest in nitrogenous matter and water and poorest in starch. The proportion of starch in the cortical layer may be twice as great as in the innermost layer, whilst, in the latter, the amount of nitrogenous matter may be 28 p.c. higher than in the cortical layer. They state that the culinary value of potatoes is directly proportional to the quantity of nitrogenous matter and inversely proportional to the amount of starch present, and that it may be measured by the ratio between these quantities. The power of the tubers to retain their shape and size when boiled in water is determined by the proteids present and is not dependent upon the proportion or size of the starch grains or the amount of pectin substances present. The resistance to swelling up

when boiled is measured by the ratio, proteid : starch, which in good varieties varies between 1 : 14 and 1 : 8.6, while in the varieties which disintegrate most it is 1 : 6 or even 1 : 4.

For culinary purposes, the aim is to select varieties with a thin cortical layer and therefore varieties with a thin cortical layer and a high content of starch are to be preferred.

New varieties of potatoes are continually being produced, for some of which great advantages are claimed.

In 1901, a wild plant growing in Uruguay, which was first described in 1767 by Commerson, was brought to Europe by Heckel. By cultivation, an edible tuber, equal to the ordinary potato, has been obtained, which it is claimed is immune to ordinary potato diseases, more resistant to frost, and capable of yielding enormous crops. This plant is known as *Solanum Commersonii* (Dun.) and is characterised by the large number of aerial tubers which it produces, in addition to its subterranean ones (Labergerie. Bied. Zentr. 1905, 34, 616).

The ash of potatoes, according to Wolff, contains on the average—

K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	SiO <sub>2</sub>	Cl
60.3	2.6	2.6	4.7	1.2	17.3	6.4	2.0	3.0

Potatoes are used as human food, as food for animals (best after boiling), and as a source of starch.

As a food for animals, potatoes are used raw, steamed, as silage, or, recently, dried. The following figures (Kellner) show the composition of these various forms:—

—	Water	Protein	Fat	N-free extract	Fibre	Ash
Raw, medium	75.0	2.1	0.1	21.0	0.7	1.1
„ watery	83.0	1.6	0.1	13.9	0.6	0.8
„ dry	74.0	2.1	0.1	21.9	0.8	1.1
Steamed	66.5	1.5	0.1	30.1	0.8	1.0
Raw, as silage	73.5	2.2	0.5	21.7	0.7	1.4
Dried	12.0	7.4	0.4	74.0	2.3	3.9

The haulms and 'apples' (fruit) of potatoes contain, usually, sufficient solanine to render them poisonous. They should not be used as food for animals.

Potatoes grow best in deep soils, well drained, free from acidity, and well supplied with potash and nitrogen.

For examples of the efficiency of spraying potato plants with copper compounds as a preventative of blight, v. Leaflet 14 of the Dept. of Agric. and Techn. Instruction for Ireland.

H. I.

#### POTATO OIL v. FUSEL OIL.

#### POTATO STARCH v. STARCH.

#### POTTERY and PORCELAIN.

The term 'pottery' is a very elastic one, and is used to indicate any article (or of a mixture of clays and other mineral substances), and hardened by the application of fire. In this sense the term includes all kinds of crockeryware and such common articles as flooring and roofing tiles, drain-pipes, bricks, and crucibles; nor is there any reason why this

